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ELEMENTS OF CHEMISTRY,

INCLUDING THE

ACTUAL STATE AND PREVALENT DOCTRINES OF THE SCIENCE.

BY THE LATE

EDWARD TURNER, M.D. F.R.S. L. & E.

EIGHTH EDITION.

EDITED BY

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PART II.—ORGANIC CHEMISTRY.

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THE present Edition of TURNER'S ELEMENTS OF CHEMISTRY is formed on the same plan as the last, the Seventh Edition, in which the Editors endeavoured to supply the student with a condensed view of the actual state of the science, more especially of the Organic department, which, in consequence of the rapid progress of discovery, it was necessary in that Edition entirely to re-write.

The favourable reception of that attempt to make the student acquainted with the state and prospects of the science, has rendered it necessary to publish a New Edition; and in doing so, the Editors, while adhering to the general plan of the last, have introduced all such new facts as appeared to them sufficiently established, and have thus made a very large number of additions and corrections in almost every section. They have, however, considered it of greater importance to explain clearly the admitted principles of the science, than to accumulate details.

In the department of Inorganic Chemistry many sections have been re-written, in order to attain the object in view, namely, an accurate although condensed account of the actual state of the science, of its useful applications, and of its present prospects.

Since the publication of the last Edition, many Continental chemists, including Liebig, Wöhler, Gmelin, and their numerous pupils, have finally adopted the British equivalents or atomic weights for those substances in regard to which a difference existed, as pointed out in the Preface to the Seventh Edition. This difference, therefore, no longer exists, as far as concerns the chemists above named, and many others, who, in their works, now admit, as we do, water to be HO , not as formerly H_2O ; and chloride of potassium to be KCl , and not as formerly KCl_2 , &c. In short, the atomic weights of Hydrogen, Nitrogen, Chlorine, Bromine, Iodine, and Fluorine are now, by those chemists, assumed to correspond with their equivalents, where formerly the equivalent was made to contain 2 atoms.

It is very gratifying to the Editors, that, anticipating this change on the part of the Continental chemists, they did not, in the last Edition, confuse the student by any attempt to obtain uniformity; but,

as they could perceive no good reason for the system adopted by Berzelius, of making a distinction between equivalents and atoms, (more especially after the discoveries of Dumas and Mitscherlich had shewn that the combining volume of gases could furnish no criterion for the number of atoms forming an equivalent,) waited with confidence for the time when the simple and natural principle adopted in this country should be recognized and adopted on the Continent.

One change has been made in this Edition, that, namely, of doubling the equivalents of Phosphorus, Arsenic, and Antimony, as is now done by most chemists, both here and abroad. The effect of this change is to simplify formulæ, substituting, for example, for such as P_2O_5 , As_2O_3 , and Sb_2O_3 , the more simple formulæ of PO_5 , AsO_3 , and SbO_3 . It seems now to be generally admitted, that, in the case of these elements, there is no good reason for using the smaller equivalent, and thus, in all their compounds, assuming 2 eq. of phosphorus, &c.

In the Organic Chemistry, several of the most important sections have been much enlarged, altered, and, in some cases, almost entirely re-written, so as to include the results of recent investigations. The sections on the Platinum bases, on Benzoyl, on Uric acid, on the Oily and Fatty acids, on the compounds derived from Lichens, on Indigo, on the Organic Bases, on Naphthaline, on the Albuminous compounds, on the Juice of Flesh, and, finally, the remarks on the changes which occur in vegetables and in animals, may be referred to, in proof of the anxiety displayed by the Editors to render the work what it professes to be, a clear, connected, and faithful, though brief, summary of the present state of our knowledge.

In conclusion, it is hoped that the present Edition may be found by the student to supply him with as full and accurate an account of the present state of Chemistry as is possible in a work necessarily limited in size; and that its imperfections will be ascribed to the vast extent and variety of the topics to be embraced, on most of which new researches are constantly appearing, while, on many important points, the science being obviously in a state of transition, chemists are far from being agreed as to the principles by which they are to be guided, or the modes of investigation to be pursued.

WILLIAM GREGORY.

*University of Edinburgh,
Sept. 17th, 1847.*

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PART III.

CHEMISTRY OF THE COMPOUND RADICALS;
OR, ORGANIC CHEMISTRY.

ORGANIC Chemistry is that department of the science which treats of the composition, properties, and uses, as well as of the origin, of all substances produced in the animal and vegetable kingdoms, and of the artificial compounds arising from their decomposition.

The organic kingdoms of nature are, in a great measure, formed of the same elements as the mineral or inorganic kingdom; but, in the former, a distinguishing character is the preponderance of carbon, all organic products containing a large proportion of this element, combined chiefly with hydrogen, oxygen, and nitrogen, so that these four elements are called, by way of distinction, the organic elements.

But while the four elements just mentioned constitute the great mass of every plant and animal, yet they are very far from being the only elements necessary for the existence of organized beings. About twelve other elements, namely, phosphorus, sulphur, chlorine, iodine, fluorine, silicon, calcium, potassium, sodium, magnesium, iron, and manganese, are of constant occurrence in both plants and animals; and, although their quantity, compared with that of the four chief organic elements, is very small, yet, with the exception perhaps of manganese, they are equally essential to the existence of the organized bodies in which they are found. All of them are not, however, present in every case; on the contrary, some of them evidently replace each other; but, without a certain number of these elements, no plant or animal can exist.

Thus, without phosphate of lime, which contains phosphorus and calcium, no bones could be formed; and the same salt is not less essential to the growth of plants, and especially to the formation of the seeds. Again, without silicate of potash, which contains silicon and potassium, no graminaceous plant whatever can grow. Without sulphur, as well as phosphate of lime, no nutritious vegetable capable of yielding blood to the animal body can thrive; and the most lavish supply of the four organic elements cannot support life, whether animal or vegetable, unless it is accompanied by the other elements of which we have spoken, and which, being derived from the soil, and being, from their fixed nature, indestructible by fire, and thus recovered in the

ashes of a plant or animal, are called the mineral or inorganic constituents of animals and vegetables.

It will be seen that the fifteen or sixteen elements above mentioned as occurring in the organic world are the same which constitute the great mass of the mineral world, with the exception of aluminum, which is very abundant in minerals, and which hardly ever occurs in organic bodies, being probably accidentally present when it is found. As the organic world is characterised by the predominance, in quantity, of carbon, so the mineral or inorganic world is marked by a similar predominance of silicon, and by the very great abundance of chlorine (in sea-salt), and of the metals sodium, aluminum, calcium, and iron. Oxygen, hydrogen, and nitrogen are very abundant in all the kingdoms of nature.

It is thus evident that organic chemistry is not essentially different from inorganic chemistry, so far as the nature of the elements is concerned. But there is a peculiarity in the mode in which the chief elements of organic nature are combined together; and it is this which we express by the term "Chemistry of Compound Radicals."

By the term "compound radical" is denoted a certain class of compound bodies possessing the property of uniting with the elements, and of forming with them combinations, which are analogous in their properties to the combinations of two simple bodies; combinations therefore in which the elementary body may be removed, and its place occupied by the equivalent quantities of other simple bodies.

The compound radicals are capable of uniting with each other; they form, with oxygen and sulphur, acids and bases; many of them unite with hydrogen, producing *hydracids*.

Were our knowledge of organic chemistry more complete than it yet is, all organic compounds would probably admit of being arranged in groups, of each of which groups a compound radical would form the origin; the individual members of these groups arising from the combination of this radical with elementary bodies, and from the union of the compounds thus formed with other compound bodies.

It is not meant to assert that in all cases these radicals actually exist; but it is certain that some such bodies are known, as, for example, cyanogen and cacodyle, which have been obtained in the separate state, and whose compounds are perfectly analogous to those of chlorine and of metals. In other cases the radicals are quite unknown in the separate state, but the perfect analogy of the compounds with those of the known radicals renders their existence highly probable. Finally, in many cases, our knowledge of the compounds constituting a group

is not sufficient to enable us to draw any conclusion as to the existence or composition of the radical. But wherever our acquaintance with compounds of a group is such as to entitle us to assume a radical for its foundation, the assumption, even if considered merely as an aid to the memory, in classifying a large number of complex details, will be found of great assistance to the student. It is chiefly with this view, therefore, that the theory of compound radicals is here adopted; and, as far as such radicals may be fairly admitted, our arrangement will be founded upon it.

It is by the assumption of compound radicals, that we are enabled to explain the numerous cases of isomerism and polymerism which occur in organic chemistry. Thus, for example, the three compounds aldehyde, acetic ether, and butyric acid, are polymeric, the two latter isomeric, the empirical formula of aldehyde being $C_4H_4O_2$, and that of the others $C_8H_8O_4$. In the following tabular view the rational formulæ are contrasted with the empirical formulæ, and although in the case of butyric acid no radical is known, it is evident that when discovered it will greatly facilitate the recollection of the facts.

	Empirical Formulæ.	Rational Formulæ, Full.	Rational Formulæ, Condensed.
Aldehyde	$C_4H_4O_2$	$(C_4H_3)O, HO$	$AcO, HO.$
Acetic Ether	$C_8H_8O_4$	$(C_4H_5)O + C_4H_3O_3$	$AcO + AcO_3.$
Butyric Acid	$C_8H_8O_4$	$C_8H_7O_3 + HO$	$(?)$

Again, alcohol $C_4H_6O_2$, and ether C_4H_5O , are believed to contain the same radical C_4H_5 , and their rational formulæ are accordingly $(C_4H_5)O$ for ether, and $(C_4H_5)O + HO$ for alcohol, which thus appears to be a hydrate of ether. And if we represent the radical C_4H_5 by $Ae = \text{ethyle}$, we have then the simple and easily remembered formulæ AeO and AeO, HO . It is not easy to remember such formulæ as $C_{18}H_{10}O_4$ or $C_6H_6NAs_2$. But if we are told that the former is benzoic ether, $(C_4H_5)O + C_{14}H_5O_3 = AeO + BzO$, Bz being benzoyle the radical of benzoic acid, and that the latter is the cyanide of cacodyle, $C_4H_6As_2 + C_2N = KdCy$, Kd being the radical cacodyle $C_4H_6As_2$, we find them easy to comprehend as well as to recollect.

But while we find the assumption of the existence of compound radicals so advantageous in studying organic compounds, we must not forget, that, although more frequent in this department, compound radicals do not exclusively belong to organic chemistry. We have seen that it is highly probable that the radicals of sulphuric, phosphoric, and nitric acids, as well as of many other acids, are compound, and we find, moreover, that these supposed radicals are very analogous to the simple radicals chlorine and its analogues.

The following table will exhibit some of the radicals, simple and compound, both inorganic and organic, with one or two of their chief compounds, by which it will be seen that we only extend farther in organic chemistry an idea already familiar in inorganic chemistry, although it is true that the first observed compound radicals were of organic origin.

ACID RADICALS.

Name.	Symbol.	Hydrogen Acid.	Potassium Salt.	Silver Salt.
Chlorine	Cl	HCl	KCl	AgCl.
Radical of Sulphuric Acid	SO ₄	HSO ₄	KSO ₄	AgSO ₄ .
Radical of Nitric Acid	NO ₆	HNO ₆	KNO ₆	AgNO ₆ .
Cyanogen, C ₂ N	Cy	HCy	KCy	AgCy
Sulphocyanogen, C ₂ NS ₂	CyS ₂	HCyS ₂	KCyS ₂	AgCyS ₂ .

BASIC RADICALS.

Name.	Symbol.	Protoxide.	Hydrated Protoxide.	Chloride.	Sulphuret.
Potassium	K	KO	Ko,HO	KCL	KS.
Ammonium, NH ₄	Am	AmO	AmO,HO	AmCl	AmS.
Ethyle, C ₄ H ₅	Ae	AeO	AeO,HO	AeCl	AeS.
Methyle, O ₂ H ₃	Me	MeO	MeO,HO	MeCl	MeS.
Cacodyle, C ₄ H ₆ As ₂	Kd	KdO	KdO,HO	KdCl	KdS.

There are other kinds of organic compound radicals, not falling under either of the two classes above given; such as benzoyle C₁₄H₅O₂ = Bz, and cinnamyle C₁₈H₈O₂₁, which form acids with oxygen, and volatile oils with hydrogen. These have no precise inorganic analogues, but it is evident that compound radicals are not confined to organic chemistry. Besides, we have no absolute certainty that even chlorine and potassium are simple; and the characters and relations of cyanogen and cacodyle are such, in every particular, that the former must be classed with chlorine, and the latter with potassium. Indeed, were it not that we can easily decompose both, their relations to other bodies would lead us to class them with elementary bodies. The tables above given will speak for themselves, and show the perfect analogy between the relations of the simple and those of the compound radicals.

If from any of these combinations one or more of their constituent parts be removed, a new compound of another radical, and sometimes also a new radical in the free or uncombined state, is produced; thus the bisulphuret of cyanogen is decomposed by a temperature of 266° into bisulphuret of carbon, sulphur, and mellone; — 4 at. bisulphuret of cyanogen = N₄C₈S₈ is decomposed into C₂S₄ (2 at. of bisulphuret of carbon), S₄ and N₄C₆ (mellone). Here the bisulphuret of carbon is a new compound of a simple radical, carbon; and mellone is a new compound radical, analogous to cyanogen in containing the same ele-

ments, and forming with the elementary bodies a series of compounds analogous to those of cyanogen. Alcohol from which two atoms of hydrogen have been withdrawn gives rise to aldehyde; ($\text{C}_4\text{H}_5\text{O} + \text{aq.}$) $- 2\text{H} = \text{C}_4\text{H}_3\text{O} + \text{aq.}$ Here alcohol, the hydrated oxide of the radical C_4H_5 (ethylc), by losing 2 at. hydrogen, yields aldehyde, the hydrated oxide of a new radical C_4H_3 (acetylc).

When the oxygen of any organic compound has been removed, and its place occupied by its equivalent of sulphur, a sulphur-compound of the same radical is formed, and its properties are similar to those of the oxygen-compound. For example, alcohol $\text{C}_4\text{H}_5\text{O} + \text{HO}$ gives mercaptan $\text{C}_4\text{H}_5\text{S} + \text{HS}$. Here the formulæ sufficiently show the analogy in composition; and the properties and chemical relations of mercaptan are very similar to those of alcohol, as will be hereafter shewn.

Cyanic acid $\text{CyO} + \text{HO}$, when its oxygen has been replaced by sulphur, gives hydrosulphocyanic acid $\text{CyS} + \text{HS}$. Here, again, besides the analogy of the formulæ, we find a close correspondence in properties. Both compounds are acids, and their salts have the same relation to each other as that which is found between inorganic oxygen and sulphur-salts of the same acid radical; in the case, for example, of the salts of carbonic acid CO_2 , and those of carbosulphuric acid (bisulphuret of carbon) CS_2 .

When the hydrogen of an organic compound is displaced, and its position occupied by its equivalent of chlorine or oxygen, there will be formed either a similar compound of a similarly constituted radical, or several new compounds of a more simple radical.

Aldehyde acted on by chlorine forms hydrochloric acid and chloral.

$\text{C}_4\text{H}_5\text{O} + \text{aq.}$ with $\text{Cl}_6 = 1$ at. of chloral $\text{C}_4\text{Cl}_3\text{O} + \text{aq.}$ and 3HCl . Here chloral is obviously the oxide of a new radical C_4Cl_3 , the constitution of which is similar to that of the radical C_4H_3 , of which aldehyde is the oxide; and both the oxide and chloride are further similar in being combined with an atom of water, forming hydrates.

Anhydrous sugar $\text{C}_{12}\text{H}_9\text{O}_9$, in which the 9 at. hydrogen are replaced by 9 at. oxygen, is converted (by being treated with permanganate of potassa) into 6 at. of oxalic acid; for, if the hydrogen be replaced by its equivalent of oxygen, we obtain $\text{C}_{12}\text{O}_9\text{O}_9 = \text{C}_{12}\text{O}_{18} = 6\text{C}_2\text{O}_3$. C_2O_3 is the formula of oxalic acid, which is the oxide of a more simple radical.

In like manner, alcohol $\text{C}_4\text{H}_5\text{O} + \text{aq.}$ in which the 5 at. of hydrogen are replaced by 5 atoms of oxygen, gives rise to 2 atoms of oxalic acid.

The preceding examples of the replacement of one element by an-

other furnish illustrations of what is called the Theory of Substitutions, a theory which has of late years attracted much attention, especially among the French chemists, and which, originating with Laurent, has been chiefly supported by the labours of that distinguished chemist, and by those of his countrymen Dumas and Gerhardt.

The researches of these, and of other chemists, have made known to us a very large number of instances in which one of the elements of an organic compound is replaced—first, to a small extent; subsequently, to a greater degree; and finally, in some cases, altogether—by another element, while the general character, or type as it is called, of the compound remains unaltered.

For example, Dumas has shewn that the hydrogen in acetic acid $C_4H_3O_3 + HO$, may be entirely replaced by chlorine, forming the compound $C_4Cl_3O_3 + HO$, which retains the same type, being an acid, the chloracetic acid. We have seen above the same substitution of chlorine for hydrogen in aldehyde, a lower oxide of the same group as acetic acid.

Innumerable similar substitutions are now known to chemists, and constitute a series of facts of very high interest. We shall have very frequent occasion to refer to them, and in the meantime it may be pointed out that it is certainly a truly remarkable fact that the highly electro-negative chlorine, so opposed in its relations as it usually appears to be to the electro-positive hydrogen, should take its place without altering the type of the compound (using the word type as above explained). This would seem to indicate that, contrary to what is generally seen in inorganic chemistry, the chemical character of the compound does not depend so much on the *nature* of its elements, as on their *arrangement* or position in the compound.

The following considerations may serve to illustrate the present views of chemists in regard to substitutions. Almost every chemical action is a case of substitution. Thus, when water is decomposed by potassium, that metal is substituted for the hydrogen of the water. Again, a type, in inorganic chemistry, is the general formula for a large class of analogous compounds. Thus, HX is the general formula or type of a class of acids of which hydrochloric acid HCl , is an example. X represents the acid radical, simple or compound, as the case may be. In hydrochloric acid $X = Cl$; but in oil of vitriol, viewed as a hydrogen acid, H_2SO_4 , $X = SO_4$; and in hydrocyanic acid H_2C_2N or HCy , $X = C_2N$ or Cy . ΔX is the general formula or type of the class of compounds of which sea-salt, $NaCl$, is an example, and will of course include such bodies as Na_2SO_4 , $NaCy$, &c.

Nay, if Δ be made to assume a more general signification, and to

include both hydrogen and metals, the type ΔX would represent both the classes of compounds above mentioned.

Now, in any individual compound of the general formula or type ΔX , either of the elements may be replaced by another element, and this is substitution. In sea-salt, for example, NaCl , the X , in this case chlorine, may be replaced by bromine, iodine, fluorine, sulphur, selenium, SO_4 , NO_6 , cyanogen, &c., while the type remains unchanged; all the compounds, NaBr , NaI , NaF , NaS , NaSe , Na_2SO_4 , Na_2NO_6 , NaCy , belonging to the same type as NaCl .

Moreover, the Δ , in this case sodium, in sea-salt may also be replaced by hydrogen and by other metals, as potassium, barium, calcium, lead, silver, &c., and we obtain the compounds HCl , KCl , BaCl , CaCl , PbCl , AgCl , &c., still belonging to the same type.

Lastly, if both the elements Δ and X of sea-salt NaCl , are replaced by others, we obtain a still more extended series of compounds still belonging to the same type, such as KI , PbS , HCy , BaSO_4 , AgNO_3 , CaF , HgBr .

Here, then, without leaving the well-marked saline or acido-saline type ΔX , we have an immense number of individuals which, while each exhibiting the typical character, perfectly exemplify also most extensive substitutions. And in this sense, as before stated, almost every chemical action is a case of substitution of one element for another.

But in inorganic chemistry we observe one fact, which, if not invariable, at least constitutes a rule with but few exceptions. It is this: that an element representing Δ in the general formula is replaced only by another substance representing Δ , and so of X likewise. Thus, sodium, which in sea-salt represents Δ , can be replaced only by hydrogen and by metals which also stand for Δ ; and chlorine, the representative of X in sea-salt, can be replaced only by bromine, iodine, &c., in short, by other representatives of X . It will be observed that Δ stands for the electro-positive, and X for the electro-negative elements.

It is true that a very few cases occur in inorganic chemistry, where a body of the class Δ seems to be replaced by another of the class X , without alteration of the type. Thus, sulphur and chlorine belong to the class X , and manganese to the class Δ . But there are two compounds of manganese, the manganic and permanganic acids, in which the manganese not only occupies the place of Δ , that is, the electro-positive ingredient which is natural to it as to metals in general, but at the same time appears to replace sulphur and chlorine; or,

what comes to the same thing, in sulphuric and perchloric acids, sulphur and chlorine play the part of Δ , while in general they play that of X. Sulphuric acid SO_3 , and manganic acid MnO_3 , appear to be isomorphous and to belong to the same type, as do perchloric acid ClO_7 , and permanganic acid Mn_2O_7 . So that an element does occasionally, even in inorganic chemistry, assume both characters, that of Δ as well as that of X, and, under both forms, replace another element without changing the type. Sulphur replaces chlorine in the protochloride of iron FeCl , yielding FeS , a body of the same type; and sulphur also replaces manganese in manganic acid MnO_3 , yielding SO_3 , a body also of the same type. In the former the sulphur represents X, in the latter Δ .

On the electro-chemical theory, these cases are explained by considering sulphur as positive or Δ with respect to oxygen, and negative or X with respect to metals. But we have no examples of any bodies acting this double part in inorganic chemistry, except such as, like sulphur and chlorine, occupy a place intermediate between oxygen and the metals.

But in organic chemistry we find a new kind of substitution, utterly at variance with the electro-chemical theory; and it is this which is more particularly understood by the term "substitution." We have chlorine taking the place of hydrogen, a body to which, on the electro-chemical view, it is entirely antagonistic, and this, too, without changing the type. Examples have been given above, and there is no doubt that the same is true of bromine, iodine, and other substances. In these cases, therefore, as we cannot suppose the electro-chemical nature of the element to be that on which depend the properties of the type, we are compelled to look to another source for those properties, and this can only be the peculiar relative position or arrangement of the elementary molecules.

The very striking facts ascertained by Laurent in his researches on naphthaline will be found to throw much light on this interesting subject, and to promise at some future period a far higher degree of insight into the constitution of matter than we at present possess.

But while we admit the importance of the doctrine of substitution as embodying a vast array of important facts, it is necessary to mention that the distinguished French chemists above alluded to appear to have extended their theoretical notions on this subject further than seems warranted by facts; and, in particular, appear to conceive that the facts of substitution are in some way inconsistent with the idea of the existence of compound radicals. Now this does not appear to be at all the case. It is certain, as stated above, that some compound

radicals do exist possessing all the properties of elementary radicals; and even in the case of those radicals whose existence is hypothetical, it is not easy to see how the facts of substitution should be incompatible with their existence. We shall, therefore, avail ourselves of all the facts connected with substitution, without, on that account, either adopting all the theories of substitution, or rejecting those views of the existence of compound radicals which, in the present state of our knowledge, so materially facilitate the classification of the details of organic chemistry.

All combinations of compound radicals which do not contain nitrogen, are reduced when exposed to the action of oxygen to oxides of more simple radicals, the higher or lower degree of oxidation being dependent upon the quantity of oxygen present. Thus, by treating alcohol with oxidizing agents, acetal, aldehyde, acetic and formic acids, oxalic acid, carbonic acid, and water may be formed; as the following statement will show.

Alcohol $C_4H_5O + aq.$ is the hydrated oxide of the radical ethyle C_4H_5 ; acetal contains aldehyde; aldehyde $C_4H_3O + aq.$ is the hydrated oxide of the radical acetylene C_4H_3 ; acetic acid $C_4H_3O_3 + aq.$ is a higher degree of oxidation of the same radical; formic acid $C_2HO_3 + aq.$ is the corresponding degree of oxidation of another radical formyle C_2H ; oxalic acid C_2O_3 is the oxide of another radical C_2O_2 ; or it may be viewed as simply a sesquioxide of carbon; carbonic acid CO_2 is a higher degree of oxidation of carbonic oxide CO , or of carbon simply; and water is the oxide of hydrogen. The two last are, under every circumstance, the products which terminate the action of an excess of oxygen on organic substances.

Organic compounds not containing nitrogen may be decomposed in three different ways when brought into contact with concentrated or anhydrous sulphuric acid: firstly, the acid may withdraw water from the compound, or at least oxygen and hydrogen in the proportion in which they form water; in this case, the other component parts unite into one or more new compounds; thus oxalic acid, acted on by sulphuric acid, gives rise to the formation of water, of carbonic oxide, and of carbonic acid; $C_2O_3 + aq. = CO + CO_2 + aq.$; or, secondly, the acid may at the same time give oxygen to a part of the carbon of the compound, when products analogous to the above, together with sulphurous acid, will be produced; or, thirdly, the acid may give oxygen to the hydrogen of the compound, and in this case be converted into hyposulphuric acid, which usually enters into very intimate combination with the organic substance thus modified. Instances of both the latter cases will be frequently mentioned hereafter.

Hydrates of organic oxides of basic qualities, when decomposed by an ox-acid, unite with the latter, the water of the hydrate being at the same time liberated. Thus, when oxalic acid $C_2O_3 + aq.$ acts on alcohol $C_4H_5O + aq.$ (hydrate of oxide of ethyle), water is set free, and oxalic ether $C_2O_3 + C_4H_5O$ is formed. By the action of an hydracid upon the same bodies, a similar decomposition occurs, but it implies the reduction of the oxide; a compound of the radical of the oxide with the radical of the hydracid is produced, while the oxygen of the former unites with the hydrogen of the latter, forming water. Thus, alcohol $C_4H_5O + aq.$, when acted on by hydrochloric acid HCl , yields chloride of ethyle C_4H_5Cl , and water HO , the water of the alcohol being at the same time set free.

When the action of nitric acid upon an organic compound is of such a nature that only a part of the hydrogen of the latter is removed or is oxidized, it sometimes happens that a new compound, which contains all the carbon of the organic substance, is formed with one of the lower oxides of nitrogen. Some such instances will be hereafter mentioned.

By the action of strong acids upon substances containing nitrogen, there is frequently produced through the medium of the constituents of water, on the one hand ammonia, which combines with the acid, and on the other an oxide of a new radical, in which all the carbon of the original compound is present. For example, hydrocyanic acid H, C_2N , with 1 at. hydrochloric acid HCl , and 3 at. water $3HO$, forms 1 at. hydrochlorate of ammonia (sal-ammoniac) NH_3, HCl , and 1 at. formic acid C_2HO_3 . Again, oxamide $C_2O_2NH_2$, with 1 at. sulphuric acid SO_3 , and 2 at. water $2HO$, produces 1 at. sulphate of ammonia NH_3, HO, SO_3 , and 1 at. oxalic acid C_2O_3 . This kind of reaction is very frequent, and of great importance.

All organic compounds not containing nitrogen are decomposed by being fused with hydrate of potash, and if the latter be present in sufficient quantity, the decomposition is not attended with the separation of carbon; the products which are formed are the same as those resulting from the action of powerfully oxidizing agents; water is generally decomposed, its oxygen unites with the carbon and hydrogen of the substance, while its hydrogen is liberated, and either escapes in the form of gas or enters into some new combination. The resulting products of this decomposition may be either ulmic, acetic and oxalic acids, oxalic acid alone, or solely carbonic acid, according to the degree of temperature to which the mixture is exposed. Tartaric acid $C_8H_4O_{10}$ when fused with hydrate of potash is decomposed into water

HO, oxalic acid C_2O_3 , and acetic acid $C_4H_3O_3$. Paper and wood dust give in the same way oxalic acid and free hydrogen.

All organic compounds containing nitrogen are decomposed by being boiled in a solution of caustic potash, or by being fused with the hydrate; the products are generally the same as those generated by the action of a strong acid upon the same substances, only that with potash the ammonia is liberated, while the oxide of the new carbonized radical enters into combination with the potash. Thus oxamide, when acted on by potash, with the aid of water, as above mentioned, yields ammonia and oxalic acid; but in this case the oxalic acid unites with the potash, while the ammonia escapes; whereas, in the reaction with sulphuric acid, the ammonia combines with that acid, while the oxalic acid is liberated, and is deposited in crystals. Many substances which are very rich in nitrogen are converted, with a separation of a part of the nitrogen as ammonia, and the absorption of oxygen, into cyanic acid, and this by uniting with the potash escapes further decomposition; in this case the fused residue is completely decomposed into ammonia and carbonic acid by being dissolved in a little water and boiled; a reaction characteristic of the cyanate of potash. The fusion of organic matter with caustic potash is a valuable means of limited or imperfect oxidation, when carefully performed, and has led to some interesting discoveries in animal chemistry.

When organic bodies are exposed to the destructive distillation, their constituents give rise to the production of new volatile compounds of more simple radicals, either with or without the deposition of carbon. The products vary with the temperature, which gives rise to the division of the distillation into several periods. In the first are produced organic acids of more simple radicals, carbonic acid, water, and combustible fluids, which admit of being mixed with water. In the second period, the products of the decomposition of the new substances formed during the first are generated; the acids disappear, their oxygen unites with a part of their hydrogen and carbon, forming more simple compounds, as carbonic oxide, carbonic acid, and water, a portion of the carbon is generally deposited, while the rest unites with hydrogen, giving rise to volatile or fixed oleaginous substances. In the last period, only charcoal and gases are obtained; the latter generally consisting of a mixture of carbonic oxide, olefiant and light carburetted hydrogen gases.

Substances containing nitrogen form, under the same circumstances, ammonia, and sometimes cyanic acid; in the last period, cyanogen and hydrocyanic acid.

When an organic compound is exposed to a similar decomposition

in contact with a strong base, which is not reduced to the metallic state, or deprived of carbonic acid by a red heat, it is generally decomposed into carbonic acid, which remains in combination with the base, and into one or more new substances. Should these latter contain oxygen, they may be entirely deprived of it by a new distillation with the base, the oxygen giving rise to another portion of carbonic acid, while the other constituents of the substance are obtained in the form of solid, fluid, or gaseous compounds of carbon and hydrogen.

The action of heat on organic substances is peculiar, and furnishes an important character. As they all contain much carbon, united with oxygen, hydrogen, and nitrogen, three gaseous bodies, which also form gaseous compounds with carbon and with one another, the action of heat, in close vessels, necessarily dissipates in gaseous forms all the hydrogen, oxygen, and nitrogen, with as much carbon as they can carry off in combination. Hence, as in the destructive distillation just described, there are formed many gaseous and volatile products, while the excess of carbon appears as charcoal. For this reason all organic compounds, with a very few exceptions, such as oxalic acid and oxalates, formic acid and formates, and some others containing the largest proportion of oxygen, are blackened or charred when heated in a tube, and by this character the presence of organic matter may be detected in mixtures, &c.

TRANSFORMATIONS OR METAMORPHOSES OF ORGANIC COMPOUNDS.

Besides the decompositions and changes produced in organic compounds by the various methods above described, as by the action of oxygen, of chlorine, of acids, and of bases, and those produced by heat, there is another and a very important class of changes to which they are subject, and which frequently occur spontaneously. These are often called transformations or metamorphoses, and although strictly speaking those terms apply to all chemical changes, yet we may use them in a more limited sense, to designate those decompositions which take place spontaneously, and which are not caused by the violent action of a foreign body, often occurring without the addition of any such body, and seldom requiring more than the access of air for a time, and the presence of a ferment, or a substance which acts by its presence, but does not by its elements contribute to the formation of the new products.

The processes usually included under this head are, fermentation, including putrefaction, and eremacausis or decay.

These processes are of the utmost importance, because not only they are employed for useful purposes in the arts, but they also serve in the economy of nature to resolve dead animals and vegetables into those simpler forms of combinations of their elements which serve as food to a new generation of plants, and through them of animals. The organic elements of vegetables,—carbon, hydrogen, oxygen, and nitrogen,—are supplied to them by their atmospherical food, namely, carbonic acid, water, and ammonia; and these very compounds, carbonic acid, water, and ammonia, are the ultimate products of all processes of fermentation, putrefaction, and decay.

Were it not, therefore, for these processes, the exuviae of dead animals and plants would accumulate to an immense extent, and growing vegetables would be deprived of their proper food. In the beautiful arrangement of nature, however, these processes are ever active, forming an essential part of that wonderful yet simple chain of causes, by which the elements of the organic world are kept in a continuous circulation, successively serving as the constituents of plants, of animals, and of the air in which they live.

There is something in the very nature of the elements of organic compounds which fits them for undergoing this succession of metamorphoses. All organic compounds contain three, most of them all four of the organic elements, and having, moreover, a high atomic weight, they must of necessity have very complex molecules. If, as is probable, the smallest molecule of sugar contains $C_{12}H_{11}O_{11}$, that of stearic acid $C_{68}H_{68}O_7$, of uric acid $C_{10}H_4N_4O_6$, of indigo $C_{16}H_5NO_2$, while that of albumen contains at least $C_{48}H_{36}N_6O_{14}$ (besides a little sulphur and phosphorus) and possibly ten times more, then it is easy to see how such complex molecules, unlike the comparatively simple formulæ of inorganic nature, must possess a most unstable equilibrium, or, in other words, must be very prone to decomposition, whether from the tendency of their elements to enter into new and simpler forms of combination, or from the action of external attractions on the complex molecule.

This tendency to decomposition is particularly marked in those compounds which contain nitrogen, because that element, with weak affinities, yet forms numerous compounds with the other elements, all of which compounds are particularly prone to decomposition, and many of which undergo spontaneous decomposition. This property is well seen in the chloride and iodide of nitrogen, in the niturets of metals, in fulminating gold and silver, in the fulminates of silver and of mercury, indeed all the fulminates, in gunpowder and gun-cotton, in the nitropicrates, and other compounds of nitrogen, which explode from the slightest causes.

Now it is observed that the organic compounds which are most prone to change, and which are spontaneously decomposed, are all compounds of nitrogen. It is also ascertained that organic compounds destitute of nitrogen do not enter into fermentation, putrefaction, or decay, unless a nitrogenised body be present, which first enters into decomposition, and then acts as a ferment, exciting decomposition in the non-nitrogenised body.

This is well illustrated in the fermentation of grape juice. This fluid contains sugar, but a pure solution of sugar does not ferment. The fermentation of the sugar is here caused by the presence of an albuminous compound (a compound containing nitrogen) dissolved in the juice, which first undergoes that kind of fermentation which is called putrefaction, and when in this state excites fermentation in the sugar.

There are two theories of its action. According to that of Berzelius, it acts by contact, catalytically; that is, by contact with the sugar, it somehow causes the latter to be decomposed, just as sulphuric acid in contact with alcohol causes it to be resolved into ether and water. But this is not strictly an explanation, for it merely states the fact to be explained; and, besides, the action of sulphuric acid on alcohol is not correctly described. The acid first combines with the ether, and, on raising the temperature a little, the new compound is destroyed, and the ether distils over.

The other theory is that of Liebig. He observes, that, in innumerable cases, the contact of a body in a state of change, or of motion in the particles, causes a state of motion in the particles of another body in contact with it, and thus produces decomposition. Thus, when peroxide of hydrogen in a state of decomposition is put in contact with oxide of silver, instead of yielding oxygen to that oxide, it reduces it to the metallic state; that is, the motion of the particles of the peroxide of hydrogen being mechanically communicated to those of the oxide of silver, the equilibrium of the latter compound is overthrown, and the oxide of silver loses all its oxygen in a solution which we should have expected to yield oxygen to it. Again, nitric acid cannot dissolve platinum, but it dissolves an alloy of platinum and silver, because the particles of the silver, while entering into combination, communicate mechanically a like state to those of the platinum.

Now, when a ferment, or exciting body, comes into contact with sugar, the motion of the particles of the ferment being mechanically communicated to those of the sugar, which are held together in an unstable equilibrium, that equilibrium is destroyed, and the particles of the sugar assume new forms of combination, in this case alcohol

and carbonic acid, which are more stable under existing circumstances.

The elements of the ferment do not contribute to the formation of the new products, alcohol and carbonic acid. The ferment is itself resolved into new products, and gradually disappears. If it have disappeared before all the sugar is decomposed, then the fermentation stops until new ferment is added. In sweet wines, the ferment has been exhausted before the sugar. If, on the other hand, the sugar is all decomposed and some ferment is still present, then a new fermentation, or rather decay, sets in, and the alcohol becomes converted into acetic acid. This is the reason why weak wines are generally acid.

Such is Liebig's theory of fermentation, and it must be admitted, in the present state of our knowledge, to explain all the phenomena in a scientific manner.

The original decomposition or fermentation of the ferment of grape juice is not strictly spontaneous; for if the juice be expressed under mercury, and collected out of contact with air over that metal, it may be kept unchanged for any length of time; but if a little air be admitted, fermentation begins and cannot now be arrested. In fact, the presence of air is essential to the commencement of the change in the ferment, the oxygen of the air being absorbed. Once begun, however, the further access of air is not required.

The process of fermentation, strictly so called, as exemplified in the production of alcohol from sugar, does not directly depend on the presence of oxygen; it only requires the presence of a ferment in a state of change, a certain temperature, and a sufficient supply of water. The sugar does not increase in weight, except that cane sugar $C_{12}H_{11}O_{11}$ takes up 1 eq. of water, and thus yields 2 eq. of alcohol $2(C_4H_6O_2) = C_8H_{12}O_4$, and 4 eq. of carbonic acid $4CO_2 = C_4O_8$. But grape sugar $C_{12}H_{14}O_{14}$ (and it appears to be in this form that sugar undergoes fermentation) loses 2 eq. of water, becoming $C_{12}H_{12}O_{12} = 2(C_4H_6O_2) + 4CO_2$. It is evident, therefore, that the elements of the ferment do not contribute to the formation of the new products; and such is the case in all true fermentations.

In putrefaction the access of air is necessary, at all events to commence the process; and here the elements of the ferment or exciting body probably do contribute, with those of the putrefying body, to form some of the new products, which are very varied. This process, although essentially the same as fermentation, is commonly characterised by the offensive smell of some of the products, among which are ammonia, sulphuretted hydrogen, and perhaps phosphuretted hydro-

gen, since those bodies which are prone to putrefaction are commonly compounds containing nitrogen, sulphur, and phosphorus.

Eremacausis or decay is a slow combustion, and is throughout dependent on a supply of oxygen from the air. Any moist organic body exposed to air soon enters into eremacausis, and during this process gives out a volume of carbonic acid equal to that of the oxygen absorbed.

It would appear that it is usually the first stage of putrefaction, as well as indirectly of fermentation; for the ferment absorbing oxygen, first enters into decay, and then, if air be excluded, into putrefaction; while, if sugar or any fermentescible body be present, fermentation is excited in it.

The decay of wood, and the production of mould from dead leaves, are good examples of eremacausis; as are also the conversion of alcohol into acetic acid, and that of pyroxylic spirit into formic acid, which, although sometimes called fermentations, are cases of pure oxidation.

Putrefaction is best seen in animal matter first exposed to the air and then shut up. It is merely decay, going on either without any supply of oxygen from the air, or with a very limited supply. It is also well exemplified in the spontaneous changes which occur in a solution of cyanogen in water, in which case the four organic elements being present, there are produced ammonia, hydrocyanic acid, cyanic acid, oxalic acid, urea, and other compounds of these elements.

A great many substances may act as ferments. Thus, in the case of sugar, it may be made to yield alcohol, or to undergo the vinous fermentation, by contact, not only with the ferment of grape juice, but with the ferment of grain, which is gluten, with blood, urine, fibrine, mucus, and even fæces. But, in some cases, a special ferment is required to produce a certain fermentation. Thus, amygdaline is only made to undergo the fermentation by which it is made to yield oil of bitter almonds and hydrocyanic acid, by the presence of the albuminous matter of the sweet or bitter almond. Again, sugar of milk $C_{12}H_{12}O_{12}$, or cane sugar, after it has taken up 1 eq. of water, and grape sugar, *minus* 2 eq. of water, in order to undergo that fermentation in which it yields lactic acid, gum, and mannite, must be in contact with cheese or caseine; and the prolonged contact of the same ferment is the only known method of exciting the butyric fermentation or putrefaction, in which the lactic acid is converted into butyric acid, with disengagement of hydrogen.

The preceding observations will show that these metamorphoses or transformations possess great interest. It is hardly possible to doubt

that many operations in the animal body depend upon some such processes; as, for example, digestion, and the formation of butyric acid in the cow from the starch or sugar of its food. As little can it be doubted that some poisons, as contagions and miasmata, act as ferments to the blood, or to substances present in it.

We shall describe, under the substances which exhibit them, all the individual cases of metamorphosis coming under this head, together with the circumstances which seem to promote, to modify, or to impede these processes.

Those substances which check fermentation, putrefaction, and decay are called antiseptics. Such are strong acids, corrosive sublimate, and other metallic salts, creosote, and arsenious acid. They appear to act by entering into firm combination with the fermentescible body, and thus opposing an obstacle to the motion of the particles. Creosote instantly combines with albumen, and arsenious acid enters into union with animal membrane.

There is another kind of metamorphosis, where two organic compounds unite to produce a third, which does not contain either of the bodies which produced it. Thus, cyanic acid and ammonia unite and form cyanate of ammonia; but this salt soon passes into urea, a body which contains neither cyanic acid nor ammonia, $\text{NH}_3 + \text{C}_2\text{NO}, \text{HO} = \text{C}_2\text{H}_4\text{N}_2\text{O}_2$. Several similar cases have recently been observed. This is a pure transformation, the urea $\text{C}_2\text{H}_4\text{N}_2\text{O}_2$ containing neither more nor less than the cyanate of ammonia. It is interesting, because urea is a product of the animal body, and because it is probable that in the animal system many analogous changes may occur. This was nearly the first case in which an organic product was formed artificially; but we are now acquainted with many other examples, such as the formation of butyric acid from sugar, of formic acid from starch, of oil of spiræa from salicine, of oil of gaultheria from pyroxylic spirit and salicine.

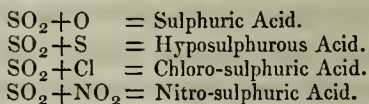
While these facts prove that we can imitate some of the results of organic life, yet their very nature shows that there are conditions in the animal and vegetable economy, which differ from those which we can command. In all these cases we only obtain one organic product from another, and the compounds which we imitate are in no case such as form a part of organic tissues. They are rather products of decomposition and excretions, such as urea, and butyric and formic acids, approaching in simplicity of constitution to inorganic products. We cannot, like plants, form organic tissues from inorganic matter; we can merely decompose some organic products, and cause some metamorphoses, but we are still as far as ever from penetrating the mys-

tery of the formation of albumen or fibrine, or the production of a cell. We cannot doubt that albumen and fibrine are chemical compounds, formed by the action of chemical laws; but these laws act under a modifying influence, namely, the vital force, and hence produce results which we cannot imitate in the laboratory, and which may for ever remain beyond our power.

THEORY OF THE ORGANIC ACIDS.

The relations exhibited in the combinations of the compound radicals have led to new and modified views of the theoretical constitution of chemical compounds in general. It has already been mentioned, that when any substance A, unites with another B, in several proportions, the quantity of B in the second compound is double, and in the third triple, of that in the first. This observation has been raised to the rank of an independent law, but upon a little closer consideration it will readily be seen that it is a necessary consequence of the law of equivalents. Thus, for example, if lead by combining with oxygen forms an oxide which has an affinity to an additional quantity of oxygen, it is impossible that the quantity of oxygen which enters into combination with the first oxide should be a fractional part of an equivalent; but it may be 1, 2, or more equivalents; or 2 equivalents of the protoxide may unite with one of oxygen, and thus a sesquioxide is obtained.

From this manner of viewing the subject, it follows as a necessary consequence, that the second atom of oxygen in the superoxide of lead must be in a state of combination different from that of the oxygen in the oxide; that sulphuric acid and peroxide of hydrogen may be considered with great probability of truth as compounds of sulphurous acid with oxygen, and of water with oxygen. Another deduction from this supposition is, that the second equivalent of oxygen in the peroxide of hydrogen, and the third in the sulphuric acid, may be removed, and their place occupied by equivalents of other simple as well as compound bodies. If the third atom of oxygen in sulphuric acid be replaced by an atom of sulphur, the formula for the hyposulphurous acid is obtained; if replaced by an atom of binoxide of nitrogen, the formula for Pelouze's nitro-sulphuric acid is obtained; if by chlorine, the compound discovered by Regnault.



If the second atom of oxygen in the peroxide of hydrogen be replaced

by an atom of chlorine, the hydrate of chlorine is obtained. If the second atom of oxygen in the peroxide of lead be replaced by an equivalent of chlorine, we obtain the oxychloride of lead $\text{Pb} \begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix} \}$.

The peroxides of sodium NaO_2 and of calcium CaO_2 yield, by a similar replacement, the bleaching compounds of soda and lime, $\text{Na} \begin{smallmatrix} \text{Cl} \\ \text{O} \end{smallmatrix} \}$ and $\text{Ca} \begin{smallmatrix} \text{O} \\ \text{Cl} \end{smallmatrix} \}$. Such compounds have lately been supposed to

be of very frequent occurrence. (Millon.) This view, therefore, not only presupposes the possibility of combinations between simple and compound bodies, but even renders their existence probable.

It will readily be observed, that the capacity of saturation of the sulphurous acid is not changed by its taking up an additional quantity of oxygen, or when this oxygen is replaced by the equivalent of sulphur or binoxide of nitrogen; on this property, therefore, these substances can have exercised no influence.

An attempt has recently been made to apply these views in explaining a certain class of phenomena which frequently present themselves when several of the mineral acids are brought into contact with certain organic combinations, and which consists in this,—that an organic compound is taken up and enters into the constitution of the anhydrous mineral acid without destroying its acid properties, or without changing its capacity of saturation. Examples of this may be seen in anhydrous sulphuric acid and naphthaline, and between the same acid and benzene. In these cases, this explanation may be employed with some degree of probability. But a large number of other compounds is known to which it cannot be applied. In the acid known as the formo-benzoic, we see a compound of formic acid with the oil of bitter-almonds $\text{C}_2\text{HO}_3 + (\text{C}_{14}\text{H}_6\text{O}_2)$, in which the capacity of saturation of the formic acid has remained unchanged. It is evident that in this substance the oil of bitter-almonds forms a constituent part of the anhydrous acid, but it has not replaced any one of the elements of the latter, as must be presupposed before the above explanation can be applied to the case.

The theoretical opinions of the nature of chloric and iodic acids first proposed by the immortal discoverer of potassium appear to afford a simple and satisfactory explanation of this and other anomalous phenomena. If these views of Davy be applied generally to all hydrated acids, certain general laws may be deduced.

I have already, in the section on salts, given a sketch of these views in a somewhat different form. The student is referred to that section, and in reading the present must bear in mind two general facts there

stated : first, that all oxygen acids, in their separate or hydrated state, contain hydrogen, which is generally viewed as forming a part of the hydratic or basic water supposed to be combined with the anhydrous acid ; and, secondly, that when a salt is formed by the action, either of what is commonly called a hydrated oxygen acid or of a hydracid, on a metallic oxide, water is uniformly separated. The formation of this water is ascribed to two different sources, by the usual theory, according as the acid employed is an oxygen acid or a hydracid. In that about to be explained, the source of this water is uniformly the same, namely, the combination of the hydrogen of the acid with the oxygen of the oxide.

I. The hydrated acids are certain compounds of one or more elements with hydrogen, in which the latter may be replaced by the equivalents of the metals.

The capacity of such an acid to neutralize a base is consequently dependent upon the quantity of hydrogen which is capable of replacement ; but upon this, the other elements of the acid, which together constitute what may be called its radical, can exercise no influence whatever. The capacity of saturation is therefore independent of the constitution of the radical.

II. When, therefore, the quantity of hydrogen in combination with the radical, and therefore replaceable, is increased or diminished, the capacity of saturation will suffer a proportional increase or diminution.

III. Should any quantities, either of the same, or of other elements, enter into the constitution of the radical, while the quantity of hydrogen which admits of replacement be unaltered, the weight of an atom of the acid will be increased, but its capacity of saturation will remain the same ; as in the case above quoted of the formo-benzoic acid. Formic acid, on this theory, is $C_2HO_4 + H$. An atom of oil of bitter-almonds $C_{14}H_6O_2$ is added to the radical, but does not affect the hydrogen which is capable of replacement, and the capacity of saturation therefore remains unchanged. The formula of the new acid is $C_{16}H_7O_6 + H$.

Salts are, according to this theory, either combinations of the metals with elements, as, for example, the haloid salts, or with compound bodies, which occupy the place of the element. They may be produced, either by bringing the element in contact with the metal (chlorine and iron), or the hydracid with the metallic oxide (hydrochloric acid with protoxide of iron, sulphuric acid $SO_4 + H$ with protoxide of iron FeO), or an oxacid (SO_3) with a metallic oxide (BaO).

In many instances, where an hydracid neutralizes a metallic oxide, no reduction occurs, or, at least, the newly-formed water is retained in

the compound; this water is in a state of combination different from that which may have united with the salt during the act of crystallizing. Such salts, when exposed to the temperature of 212° , lose their water of crystallization; but that which is produced from the oxygen of the oxide and the hydrogen of the acid is retained.

The separation of this water, and consequently the reduction of the oxide and hydracid, may nevertheless be instantly effected by bringing the salt in contact with others which are capable of forming with it a double salt. Hydrochlorate of magnesia MgO, HCl forms with sal-ammoniac (NH_4Cl), the double salt $\text{MgCl} + \text{NH}_4\text{Cl}$. Sulphate of magnesia $\text{MgO} + \text{SO}_4\text{H}$ forms with sal-ammoniac the double salt $\text{MgSO}_4 + \text{NH}_4\text{Cl}$.

The power of a base to neutralize an acid is, according to this theory, dependent not solely upon the position which it occupies in the electrical series, for of two oxides of equal basic properties, that which admits of being reduced with the greater ease will possess the greater neutralizing power. The oxide of silver ought consequently to possess this property to a greater extent than any other base; and it is a remarkable fact, that in the case of tribasic acids, such as phosphoric and meconic acids where there are 3 atoms of hydrogen capable of replacement, all the three may be replaced by silver with so much facility that the monobasic and bibasic phosphates of silver do not exist; while the tribasic phosphates of potash and soda are formed with difficulty, and the tribasic meconates of these bases are unknown except in solution. Numerous examples of this great neutralizing power of silver have been pointed out by Liebig, and they are inexplicable on the usual theory of that property in bases.

This manner of viewing the subject removes the line of distinction which has been drawn between the haloid and the oxy-salts; it is incompatible with no known fact; in organic chemistry it is of the highest importance to become acquainted with the forms in which it represents the acids and their combinations, inasmuch as it affords us a satisfactory explanation of many phenomena on which the common views can throw no light whatever.

By the term "hydrate of an acid," is meant, therefore, for the future, according to the theory now explained, combinations of one, two, three, or more equivalents of hydrogen, with certain other elements, which, being considered as combined with each other, constitute the radical of the acid. Hydrate of acetic acid is accordingly a compound of H with $\text{C}_4\text{H}_3\text{O}_4$. In the description of the compounds, however, we shall use the usual methods of representation, and consider them, according to the common view, as hydrates of anhydrous acids.

CLASSIFICATION OF THE ORGANIC ACIDS.

The organic acids may be divided into monobasic, bibasic, and tribasic acids.

The monobasic acids combine in their neutral salts with one equivalent of a base, by uniting with which one equivalent of water is separated from the hydrate of the acid. Some of the salts of the monobasic acids combine with other salts of the same class of acids, forming double salts; or with the hydrates of the acid, forming acid salts.

The acid salts of the monobasic acids are decomposed, by being mixed with a solution of other bases, into two or more neutral salts, which may be separated from each other by crystallization, provided they differ from each other in their degree of solubility, and are not isomorphous. To this class belong oxalic acid, &c.

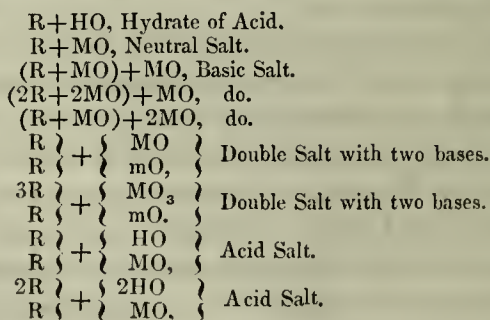
The basic salts of the same acids contain two or more equivalents of a base, by the combination of which with one atom of the acid the same quantity of water is displaced as by a single equivalent of the base.

In the bibasic acid one atom will always unite with two equivalents of a base, which separate from and occupy in the acid the position of two equivalents of water. These two equivalents of base may be, two equivalents of one and the same metallic oxide, or of two different oxides, or one equivalent of a metallic oxide, and one equivalent of a volatile base (water or oxide of ammonium).

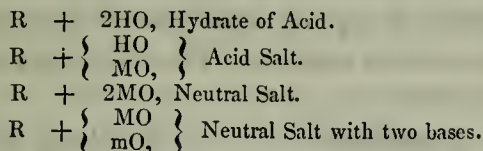
The acid salts of this class contain only one equivalent of the acid, which is the cause of there being no separation when they are neutralized by other soluble bases.

The tribasic acids neutralize three atoms of a base; for each atom of a fixed base, which unites with the acid, one atom of water is separated and its place occupied by an atom of a metallic oxide.

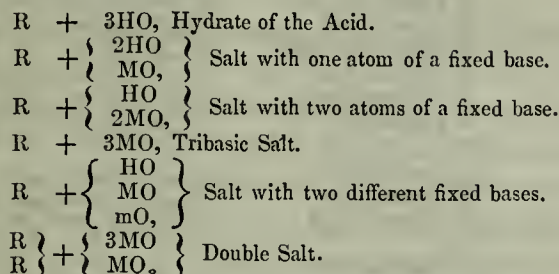
The following are the general formulæ for the salts of a monobasic acid. (R represents the anhydrous acid, MO the metallic oxide.)



General formulæ for the salts of the bibasic acids.



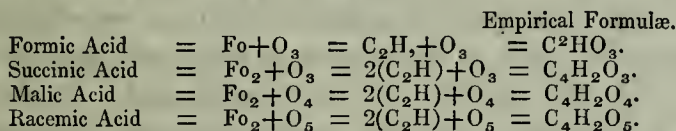
General formulæ for the salts of the tribasic acids.



The monobasic acids rarely yield, when exposed to the destructive distillation, the so-called pyrogenous acids; but whenever these do happen to be formed, they always possess the properties of a monobasic acid. The bibasic acids very generally give rise, under the same circumstances, to two new monobasic acids. Thus, gallic acid, which is bibasic, yields pyrogallic and metagallic acids, which are monobasic. The tribasic acids yield either three equivalents of a monobasic acid, or two new monobasic acids, or one monobasic and one bibasic acid. For example, when cyanuric acid, a tribasic acid, is heated, 1 eq. yields 3 eq. of cyanic acid, which is monobasic; and meonic acid, which is also tribasic, yields komenic and pyromeconic acids, the former bibasic, and the latter monobasic.

When the formulæ of certain organic acids are compared together, we are often able to trace relations which may, possibly, be entirely confined to the formulæ, and not indications of any practical connexion in their origin or mode of formation. Still there is an advantage in observing such possible relations, which may occasionally lead to the discovery of new facts, and which, at all events, serve as aids to the memory.

If we take, for example, the radical formyle $= C_2H, = Fo$, and if we suppose it combined with oxygen in various proportions, we obtain the formulæ of the following acids:—



Again, there is a most remarkable series of acids, which, when compared, are found to agree in two points: first, that each acid of the

series contains, in the hydrated state, 4 eq. of oxygen; secondly, that in each the number of eqs. of carbon and of hydrogen is the same, and in each, also, an even number. The following acids are known to belong to this series.—

1. Acetic Acid	.	$C_4 H_4 O_4 = C_4 H_3 O_3, HO.$
2. Metacetic Acid	.	$C_6 H_6 O_4 = C_6 H_5 O_3, HO.$
3. Butyric Acid	.	$C_8 H_8 O_4 = C_8 H_7 O_3, HO.$
4. Valerianic Acid	.	$C_{10} H_{10} O_4 = C_{10} H_9 O_3, HO.$
5. Caproic Acid	.	$C_{12} H_{12} O_4 = C_{12} H_{11} O_3, HO.$
6. Enanthic Acid	.	$C_{14} H_{14} O_4 = C_{14} H_{13} O_3, HO.$
7. Caprylic Acid	.	$C_{16} H_{16} O_4 = C_{16} H_{15} O_3, HO.$
8. Pelargonic Acid	.	$C_{18} H_{18} O_4 = C_{18} H_{17} O_3, HO.$
9. Capric Acid	.	$C_{20} H_{20} O_4 = C_{20} H_{19} O_3, HO.$
10. *	*	* * * * *
11. Lauric Acid	.	$C_{24} H_{24} O_4 = C_{24} H_{23} O_3, HO.$
12. Cocinic Acid	.	$C_{26} H_{26} O_4 = C_{26} H_{25} O_3, HO.$
13. Myristic Acid	.	$C_{28} H_{28} O_4 = C_{28} H_{27} O_3, HO.$
14. *	*	* * * * *
15. Palmitic and Ethalic Acids	}	$C_{32} H_{32} O_4 = C_{32} H_{31} O_3, HO.$
16. Margaric Acid	.	$C_{34} H_{34} O_4 = C_{34} H_{33} O_3, HO.$

It will be observed that one member of the series is wanting between capric and lauric acids, and one between myristic and palmitic acids; but there can be no reasonable doubt that these blanks will hereafter be filled up. As it stands, the series is one of the most remarkable known to chemists. The acids included in it are all volatile without decomposition, and their boiling point rises as the quantity of carbon and hydrogen increases. From butyric acid, No. 3, to margaric acid, No. 16, they are all oily or fatty acids; and in natural fats, as in butter, several of them are often found associated, which would indicate a common origin. The same conclusion is deduced from the recent researches of Rettenbacher, who has detected nine of the acids of this series among the products of the oxidation of oleic acid by nitric acid. We can easily see, therefore, how they may be formed in the body of the cow (five or six of them have been found in butter), by the slow and gradual oxidation of the same acid. The properties of this series of acids, as well as of their salts, are as nearly alike as their composition; that is, although acetic and margaric acids apparently differ widely in properties, as they do in composition, still there are some points of analogy even between these, the opposite extremities of the scale; while the change of properties, in passing from any one acid to that immediately on either side of it, is very slight indeed. Thus, metacetic acid is very similar to acetic acid, butyric acid to valerianic acid, and palmitic acid to margaric acid. In short, the gradation in properties is precisely equivalent to that in composition. It is also evident, that, since all these acids agree in composition only in containing 4 eqs. of oxygen, we must suppose a similarity of group-

ing or arrangement of the varying quantities of carbon and hydrogen, to account for the fact that they all, by their properties, belong to the same type.

When treating, in a subsequent section, of the changes which occur in the animal body, we shall return to this series of acids, and endeavour to trace their formation, in the animal system, from the respiratory elements of the food.

It is worthy of notice that a large number of these acids have been obtained artificially.

In the following part of the work the organic compounds will be described in the order in which they may be supposed to be developed from their radicals, whether real or hypothetical; to each compound will be attached those new products which arise from its partial decomposition, so that a number of closed groups will be formed, but the individual members of these groups will frequently admit of being deduced from other radicals, and will consequently belong to two or more of the series. This arrangement is not systematic, but it facilitates the comprehension of the changes and metamorphoses which organic substances undergo more than any other.

The known radicals of acids are,—certain compounds of *carbon* and *oxygen*, *cyanogen*, *mellone*, *benzoyle*, *cinnamyle*, *salicyle*, *acetyle*, and *formyle*.

The radicals forming bases are,—*amide*, *ethyle*, *methyle*, *cetyle*, *amyle*, and *glyceryle*.

The radicals may be distinguished as original or deduced. The latter arise out of the former, either by decomposition, as mellone from sulphuret of cyanogen, or acetyle out of ethyle; or by being doubled or tripled, as the radicals of fulminic or cyanuric acid out of cyanogen. It is very probable that both benzoyle and cinnamyle are deduced radicals.

AMIDE.

Formula NH_2 . Symb. Ad.

This hypothetical combination is considered to be the radical of ammonia. With 1 eq. of hydrogen it forms ammonia $\text{NH}_2, \text{H} = \text{NH}_3 = \text{AdH}$; and with 2 eq. of hydrogen it produces ammonium $\text{NH}_2, \text{H}_2 = \text{NH}_4 = \text{AdH}_2$. In this work the symbols NH_3 and AdH for ammonia, and those of NH_4 and AdH_2 for ammonium, will be used indiscriminately, since, as above explained, they are exactly equivalent expressions for these compounds. Ammonia may be called *hyduret of amide* or *hydramide*. In the same way as hydracids possess properties similar to those of oxygen acids, so

ammonia or hydramide, a hydro-base, has properties analogous to those of oxygen bases.

In all the compounds of ammonia, in which the acid as well as the base may be replaced by other acids or bases, both acid and base contain hydrogen. Where the acid contains no hydrogen, the compound has not the characters of a salt.

If an acid, in general, be represented by the formula XH , then the general formula of these salts is $XH, AdH = XH_2 + Ad$, or $X, Ad + H_2$. Since amide contains 2 atoms of hydrogen, every salt of hydramide should contain 4. If less hydrogen be present, the compound belongs to a different class.

When a metallic oxide is heated with a salt of hydramide, the hydrogen of the acid unites with the oxygen of the oxide, forming water, which is disengaged with the ammonia, while a metallic salt is formed. $XH, AdH + MO = XM + HO + AdH$.

If the existence of ammonium be admitted, the salts of ammonia will have the general formula X, AdH_2 , and will be compounds of ammonium with simple or compound radicals. This view has already been explained in the section on Salts. It makes the compounds of ammonium exactly analogous to those of potassium and other metals.

Ammonia, by combining with the elements of 1 at. water, produces oxide of ammonium, and we shall consider the salts of ammonia as formed of this oxide united to anhydrous acids, although it is, perhaps, more correct to consider them as compounds of ammonium with radicals. But the former view is so generally known, that it would be inconvenient at present to change it.

Ammonia.— AdH . This compound has already been described. It is formed in a variety of circumstances where nitrogen and hydrogen meet in the nascent state, especially when nitrogenized organic matters are exposed to heat.

It has the property of combining with a large number of metallic oxides, as formerly mentioned. It also combines with many chlorides, bromides, iodides, and fluorides.

It combines with many anhydrous salts, acting the same part as water of crystallization.

Ammonium.— AdH_2 . This compound has not been isolated. It has however been obtained in combination with mercury, forming the amalgam of ammonium, which has all the characters of a metallic compound. By contact with water it is resolved into mercury, ammonia, and hydrogen.

The amalgam is formed by the action of electricity on sal-ammoniac, the negative pole communicating with it through a globule of

mercurey; or by the action of an amalgam of potassium or sodium on an ammoniacal salt.

Salts of Ammonia or Oxide of Ammonium.—These have been already generally described. They are either volatile or decomposable by heat; and when treated with hydrated alkalies, yield ammonia.

They have a great tendency to form double salts with the salts of other bases, many of which have been described in the Inorganic Chemistry.

Ammonia forms with carbonic acid a great number of different compounds, which have been studied by Rose. Of these, the neutral salt, $\text{AdH}_2\text{O}, \text{CO}_2$, only exists in solution, or in combination with the others. The bicarbonate, $\text{AdH}_2\text{O}, 2\text{CO}_2 + \text{aq.}$ is the most stable. Dry ammonia and dry carbonic acid form a peculiar compound, AdH, CO_2 , which may be called the anhydrous carbonate, or, more correctly, carbonate of hydramide.

The salt commonly called sesquicarbonate is a compound of the neutral carbonate of oxide of ammonium with the anhydrous bicarbonate. Salt A, $(\text{AdH}_2\text{O}, \text{CO}_2) + (\text{AdH}_2\text{O}, 2\text{CO}_2)$. When heated, this salt yields two others, carbonic acid being given off. The first is Salt B, $3(\text{AdH}_2\text{O}, \text{CO}_2) + (\text{AdH}_2\text{O}, \text{CO}_2)$. The second is Salt C, $(\text{AdH}_2\text{O}, \text{CO}_2) + (\text{AdH}, \text{CO}_2)$. Another salt is obtained when the melted sesquicarbonate is allowed to cool; it is $(\text{AdH}_2\text{O}, \text{CO}_2) + (\text{AdH}_2\text{O}, 2\text{CO}_2) + 3\text{HO}$. By the action of heat on the salt B, Rose obtained it in two new forms, with 8 at. and with 1 at. water of crystallization. The last of these, when distilled, yields the bicarbonate with 2 at. water; and this, when heated, gives another new salt, $4\text{AdH}_2\text{O} + 7\text{CO}_2 + 8\text{HO}$, by losing 1 at. of carbonic acid. When a solution of sesquicarbonate is evaporated in vacuo near sulphuric acid, crusts are formed, the formula of which is $4\text{AdH}_2\text{O}, 9\text{CO}_2, 5\text{HO}$. There are yet other forms of carbonate of ammonia, but the facts above stated are sufficient to show how great a variety of compounds may result from the combination of two substances, although such cases are rare in inorganic chemistry. But carbonic acid and ammonia both belong by their origin to organic chemistry.

COMBINATIONS OF AMIDE.

Amide combines with metals and with some compound radicals. Of the compounds with metals, those with potassium and sodium are known in a separate form. They are formed by the action of these metals on dry ammonia when hydrogen is disengaged; and when put into water they decompose it, producing potash or soda and ammonia. (Gay-Lussac and Thenard.)

The compounds of amide with radicals, when acted on by acids or alkalies, decompose water, producing an acid and ammonia. Thus, oxamide, $\text{Ad}, \text{C}_2\text{O}_2$, with water, HO , yields oxalic acid, C_2O_3 , and ammonia, AdH . This class of compounds will be described under the acids which yield them.

The compound of amide and mercury, amidide or amiduret of mercury, forms, according to Kane, compounds with the chlorides, oxides, and salts of mercury, one of which, white precipitate, has been long known, although its composition had not been previously ascertained. The following table contains some of these compounds:—

$\text{AdHg} + \text{HgCl}_2$	.	.	White precipitate.
$\text{AdHg} + \text{HgO}_2$	}	.	Formed by the action of alkalies on the above.
HgCl_2		.	
$2\text{AdHg} + 2\text{SO}_3, 3\text{HgO}_2$	.	.	Amiduret with basic sulphate of mercury.
$2\text{AdHg} + 2\text{NO}_5, 3\text{HgO}_2$	.	do. do.	do. nitrate of do.
$\text{AdHg} + \text{NO}_5, 2\text{HgO}$	.	.	Soluble mercury of Hahnemann.

Chloramide of Mercury.—Syn. White Precipitate. This compound is obtained by adding caustic ammonia to a solution of corrosive sublimate. When acted on by boiling water, or by caustic potash, it yields the second compound above mentioned, which is a compound of chloramide and deutoxide of mercury. When too little ammonia is used, there is formed another white compound, in which the salt of alembroth is combined with true white precipitate; $(\text{HgCl}_2, 2\text{AdH}_2\text{Cl}) + (\text{AdHg}, \text{HgCl}_2)$. According to Kane, protochloride of mercury forms a similar compound, which is black. Compounds of amidide of mercury with basic sulphate and nitrate of mercury are given in the table.

When ammonia is added in excess to hot solutions of the salts of copper and silver, crystallizable compounds are produced, in which the metallic amidide is combined with a salt of ammonia. These have been examined chiefly by Kane.

Sulphamide.—Under this name Regnault has described a compound, the formula of which appears to be Ad, SO_2 . When heated with acids it yields ammonia, which combines with the acid, and sulphuric acid, which can now be detected in the solution, but not before. It is obtained by exposing the new acid discovered by Regnault, chlorosulphuric acid $= \text{S} \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix}$, to dry ammonia, when sal-ammoniac and sulphamide are formed.

Sulphohydramide.—This is the compound formed by the combination of dry ammonia and anhydrous sulphuric acid. It is not sulphate of ammonia, and its formula appears to be SO_3, AdH . To form sulphate of ammonia the elements of 1 at. water are wanting. $\text{SO}_3, \text{AdH} + \text{HO} = \text{SO}_3, \text{AdH}_2\text{O} = \text{SO}_4, \text{AdH}_2$. (Rose.)

Bisulphohydramide.—This is the compound formed by the action of dry ammonia on anhydrous sulphurous acid. By the presence of water it is converted into a mixture of bisulphate and hyposulphite of oxide of ammonium. Its formula is $\text{AdH}_2\text{S}_2\text{O}_4$, which explains this change, for $2(\text{AdH}_2\text{S}_2\text{O}_4) + 2\text{HO} = (\text{AdH}_2\text{O}, 2\text{SO}_3) + (\text{AdH}_2\text{O}, \text{S}_2\text{O}_2)$. When evaporated with an excess of caustic potash, at a certain point of concentration, a sudden change occurs: sulphate of potash is deposited, and hyposulphite remains in solution.

AMIDE AND PLATINUM.

Under this head we shall briefly notice some very interesting compounds, which may be viewed as containing, or being derived from, the amide of platinum.

When protochloride of platinum PtCl is heated with ammonia, there is formed at first a green crystalline compound, called the salt of Magnus, who discovered it. It contains the elements of the protochloride and ammonia $\text{PtCl} + \text{NH}_3$, but combined in some new form, as it does not contain ammonia, as such.

If this compound be further heated with ammonia it dissolves, and the solution, on evaporation, yields white or yellowish crystals, discovered by Reiset, of the composition $\text{PtCl} + \text{N}_2\text{H}_6 + \text{aq}$. These crystals, at 212° , become anhydrous, and are then $\text{PtCl} + \text{N}_2\text{H}_6$, or they contain just twice as much ammonia as the green crystals. But here, also, the ammonia is only present by its elements, and not as such. This compound, in fact, is the chloride of a new compound basic radical PtN_2H_6 , and its formula is $(\text{PtN}_2\text{H}_6) + \text{Cl}$.

If this chloride be heated to from 265° to 290° , ammonia is formed and expelled, and there remains a yellow crystalline compound, discovered by Peyrone, the empirical formula of which is PtClNH_3 , that is, it is isomeric with the green crystals of Magnus, but differs from it in being soluble in hot water, and in exhibiting all the characters of the chloride of a second new basic radical PtNH_3 . On this view, its rational formula is $(\text{PtNH}_3) + \text{Cl}$.

The salt of Magnus is probably an ammoniated protochloride of platinum $\text{PtCl} + \text{NH}_3$, or it may be merely an insoluble modification of Peyrone's compound.

But this is not all. For it was discovered by Gros, that, if the green salt of Magnus be dissolved in nitric acid, it is decomposed, platinum being deposited, and nitrous acid given off; while the solution, in which no ammonia is found, deposits on cooling white crystalline

scales, which are the nitrate of the oxide of a third new basic radical PtClN_2H_6 . The formula of the crystals is $(\text{PtClN}_2\text{H}_6)\text{O} + \text{NO}_5$.

Two things are here especially worthy of notice. First, that this radical has the very same composition as the chloride of the radical first mentioned $\text{PtN}_2\text{H}_6 + \text{Cl}$; and, secondly, that the eq. of chlorine in these two compounds plays different parts, and that in Reiset's chloride it acts as a salt radical, while in Gros's nitrate the chlorine is a part of the radical. Nay, this last radical actually forms a chloride, which is obtained in the form of a heavy crystalline powder by adding hydrochloric acid to the nitrate, and the formula of which is $(\text{PtClN}_2\text{H}_6) + \text{Cl}$. In this chloride, we have 2 eqs. of chlorine, one acting as an electro-negative salt radical, the other as a part of the electro-positive radical united to that salt radical.

Here, then, we have three new radicals all containing platinum and the elements of ammonia, while one of them also contains chlorine.

All of these three radicals are entirely analogous in their chemical relations to ammonium, and they are, probably, like that body, compound metals. The following table will exhibit this analogy:—

Radical.	Oxide.	Chloride.	Sulphate.	Nitrate.
Ammonium NH_4 = AdH_2 = Am	$(\text{NH}_4)\text{O}$ = AmO	$(\text{NH}_4) + \text{Cl}$ = AmCl	$(\text{NH}_4) + (\text{SO}_4)$ = AMSO_4	$(\text{NH}_4) + (\text{NO}_6)$ = AmNO_6
Radical <i>b</i> of Reiset = PtNH_3 = $\text{N} \left\{ \begin{smallmatrix} \text{H}_3 \\ \text{Pt} \end{smallmatrix} \right.$	$(\text{PtNH}_3)\text{O}$ = $\text{N} \left\{ \begin{smallmatrix} \text{H}_3 \\ \text{Pt} \end{smallmatrix} \right\} + \text{O}$	$(\text{PtNH}_3) + \text{Cl}$ = $\text{N} \left\{ \begin{smallmatrix} \text{H}_3 \\ \text{Pt} \end{smallmatrix} \right\} + \text{Cl}$	$(\text{PtNH}_3) + \text{SO}_4$ = $\text{N} \left\{ \begin{smallmatrix} \text{H}_3 \\ \text{Pt} \end{smallmatrix} \right\} + \text{SO}_4$	$(\text{PtNH}_3) + \text{NO}_6$ = $\text{N} \left\{ \begin{smallmatrix} \text{H}_3 \\ \text{Pt} \end{smallmatrix} \right\} + \text{NO}_6$
Radical <i>a</i> of Reiset = PtN_2H_6	$(\text{PtN}_2\text{H}_6) + \text{O}$	$(\text{PtN}_2\text{H}_6) + \text{Cl}$	$(\text{PtN}_2\text{H}_6) +$ SO_4	$\text{PtN}_2\text{H}_6 +$ NO_6
Radical of Gros = PtClN_2H_6	$(\text{PtClN}_2\text{H}_6) + \text{O}$	$(\text{PtClN}_2\text{H}_6) + \text{Cl}$	$(\text{PtClN}_2\text{H}_6) +$ SO_4	$\text{PtClN}_2\text{H}_6 +$ NO_6

Having thus described the origin of these very remarkable compounds, we shall now briefly notice each of the three radicals in the order in which they occur in the table, which is that of the relative complexity of their formulæ, beginning with the simplest.

Radical b of Reiset.—When the hydrated oxide of the radical *a* of Reiset $(\text{PtN}_2\text{H}_6\text{O}) + \text{HO}$, is heated to 212° , the water and half of the ammonia are expelled, and there remains the oxide of the radical *b* $(\text{PtNH}_3)\text{O}$. This oxide, when heated in the air, burns like tinder, and leaves a residue of platinum. It is basic, and combines with acids,

forming salts, which have as yet been little studied, but which have the property of detonating when heated.

When the iodide of the radical α of Reiset $(PtN_2H_6)I$ is boiled with water, half its ammonia is expelled, and there is deposited the iodide of the radical b $(PtNH_3)I$. We see from this, that the radical b $PtNH_3$ acts like a metal, forming compounds with iodine and oxygen, quite analogous to the iodides and oxides of metals.

From the iodide, by the action of nitrate or sulphate of silver, we obtain the nitrate or sulphate of the new base. Thus, $(PtNH_3)I + AgNO_3 = (PtNH_3)NO_3 + AgI$, or $(PtNH_3)I + AgO,NO_2 = (PtNH_3)O,NO_2 + AgI$.

When these salts, the nitrate and sulphate of radical b , are acted on by hydrochloric acid, they yield a crystalline precipitate of the yellow compound described by Peyrone, which is the chloride of the radical b $(PtNH_3)Cl$. This chloride, as Peyrone proved, is also obtained by heating the chloride of radical α .

In all these reactions, although the radical itself has not been isolated, we see a perfect analogy between the radical b and ammonium, or, indeed, any other metal. We also observe that the oxide, chloride, and iodide of this radical may all be obtained by heating the corresponding compounds of radical α so as to expel half the ammonia they contain. Moreover, if we add ammonia to the salts of radical b , they are converted into those of radical α .

Radical α of Reiset.—This radical, like the preceding, is not yet known in the separate state. It has very strong affinities, and in its compounds exhibits a wonderful analogy not only to ammonium, which is equally unknown in a separate form, but even to potassium. Its formula is PtN_2H_6 .

The chloride of this radical $(PtN_2H_6)Cl$ is easily obtained as above described, by heating protochloride of platinum in a large excess of ammonia till it is dissolved, and evaporating the solution till it crystallizes, which it does very readily. The crystals are long prisms, commonly tinged with straw-colour, but sometimes colourless, and very soluble in water.

Like all soluble metallic chlorides, this salt precipitates nitrate of silver, and gives rise to the nitrate of the oxide of the radical. Thus, $(PtN_2H_6)Cl + AgNO_3 = (PtN_2H_6)NO_3 + AgCl$; or $(PtN_2H_6)Cl + AgO,NO_2 = (PtN_2H_6)O,NO_2 + AgCl$. The sulphate is easily obtained by acting on the chloride with sulphate of silver, or on the nitrate or chloride with sulphuric acid. Both the nitrate and the sulphate crystallize readily.

If to the sulphate $(PtN_2H_6)SO_4$, or $(PtN_2H_6)O,SO_3$, there be

added just so much baryta as precipitates the sulphuric acid, there will remain in solution the oxide of the radical. Thus, $(\text{PtN}_2\text{H}_6)\text{SO}_4 + \text{BaO} = (\text{PtN}_2\text{H}_6)\text{O} + \text{BaSO}_4$. This oxide instantly takes up water, forming a hydrate $(\text{PtN}_2\text{H}_6)\text{O}, \text{HO}$, which resembles no substance so much as it does the hydrate of potash (caustic potash, KO, HO). Its solution is strongly alkaline and caustic, having the taste of potash or soda, and giving to the fingers a soapy feel. If exposed to the air, it absorbs carbonic acid as rapidly as potash, soda, &c. do, and must, therefore, be concentrated out of contact with air, when it crystallizes as a hydrate in white prisms. It is in every respect as perfect an alkali as any known compound. It neutralizes acids, forming crystallizable salts, from which it may again be obtained unchanged. With hydrochloric or hydriodic acids, it yields water and the chloride or iodide of the radical $(\text{PtN}_2\text{H}_6)\text{O}, \text{HO} + \text{HCl} = 2\text{HO} + (\text{PtN}_2\text{H}_6)\text{Cl}$, &c.

When the hydrated oxide is heated to 212° , it loses water and half its ammonia, and leaves the oxide of the radical *b*, as above described.

When the chloride is heated to from 265° to 290° , it loses half its ammonia, and leaves the chloride of radical *b*, as has been mentioned above.

When the iodide is boiled with water it loses half its ammonia, and deposits the iodide of radical *b*, as has also been mentioned under the head of that radical.

Radical of Gros.— PtClN_2H_6 . This, which we shall call radical *c*, has the same composition as the chloride of radical *a*, but it is a totally different compound. It is not yet known in the separate state, but its compounds are perfectly analogous to those of the preceding, from which they differ only in containing 1 eq. of chlorine as a constituent of the radical or compound metal of the series.

When the green compound of Magnus PtClNH_3 (which is isomeric with the chloride of radical *b*, but is a distinct compound) is dissolved in nitric acid, platinum is deposited, and the solution on cooling deposits crystals of the nitrate of the oxide of radical *c*. Two equivalents of the green crystals, $= \text{Pt}_2\text{Cl}_2\text{N}_2\text{H}_6$, by losing 1 eq. of protochloride of platinum and taking up 1 eq. of oxygen, will give rise to the oxide of radical *c* $(\text{PtClN}_2\text{H}_6)\text{O}$.

This oxide has not yet been isolated, being probably somewhat prone to decomposition when separated, from its complex nature. It forms, however, neutral and crystallizable salts with sulphuric and nitric acids; and when these salts are acted on by hydrochloric acid, there is deposited a heavy crystalline powder, which is the chloride of radical *c* $(\text{PtClN}_2\text{H}_6)\text{Cl}$.

It has also been shewn that if a current of chlorine be passed through a solution of the nitrate of radical a , it is converted into nitrate of radical c . This is another proof that the composition of these bodies has been correctly ascertained, and that all three radicals are related; for, by adding ammonia to the nitrate of b , it is converted into the nitrate of a , which again, by taking up 1 eq. of chlorine, passes into the nitrate of c .

Such is a brief account of what is ascertained with regard to these very remarkable compounds. The following tabular view, in which they are compared with ammonium, and where the three new radicals are represented by the contractions R^b , R^a , and R^c , will perhaps be more easily understood than the fuller table above given.

Name and Composition of Radical.	Symbol.	Oxide.	Chloride.	Iodide.	Sulphate.	Nitrate.
Ammonium $NH_4 = AdH_2$	Am	AmO	AmCl	AmI	Am,SO ₄	Am,NO ₆
Radical b (Reiset) $PtNH_3 = Ad_{Pt}^H$ }	R^b	R^bO	R^bCl	R^bI	R^b,SO_4	R^b,NO_6
Radical a (Reiset) $PtN_2H_6 = PtAd_2, H_2$	R^a	R^aO	R^aCl	R^aI	R^a,SO_4	R^a,NO_6
Radical c (Gros) $PtClN_2H_6 = PtClAd_2, H_2$	R^c	R^cO	R^cCl	R^cI	R^c,SO_4	R^c,NO_6

The above table exhibits the very striking analogy between the four compound radicals, namely, ammonium, and the new platinum radicals b , a , and c . All the compounds in this table, with the exception, perhaps, of the four radicals, of the oxide of ammonium, and of the oxide and iodide of radical c , are known. Oxide of ammonium, it is well known, when isolated assumes the form of ammonia and water $NH_4O = NH_3 + HO$, and the oxide of radical c may probably be equally unstable. As for the iodide of radical c , it has probably not been formed, simply because its formation has not been attempted. The production of the chloride is so easy, that we can hardly doubt that the same method, *mutatis mutandis*, would yield the iodide.

In the first column of the table I have inserted certain interpretations of the formulæ of these radicals, which express one view that is taken of their constitution.

If ammonium NH_4 be viewed as a compound of amide NH_2 , it

will assume the form $\text{NH}_2 + \text{H}_2$, or briefly AdH_2 , or rather $\text{AdH} + \text{H}$.

Now, on the principle explained in the section on the organic acids, various elements may be conceived as added to the radical of ammonium without altering its basic power, provided the 1 eq. of hydrogen, on the position of which that power seems to depend, be not affected.

If, then, instead of the amidide of hydrogen, the radical of ammonium, we take amidide of platinum, we have the radical b , $\text{AdPt} + \text{H} = \text{PtNH}_3 = \text{R}^b$, a compound analogous to ammonium, and in which hydrogen is replaced by platinum.

The two radicals a and c are of course formed by the further addition of ammonia for the former $(\text{AdPt} + \text{AdH}) + \text{H} = \text{PtAd}_2\text{H} + \text{H} = \text{PtN}_2\text{H}_6 = \text{R}^a$; and of chlorine to this last for the latter $(\text{PtAd}_2\text{HCl}) + \text{H} = (\text{PtClN}_2\text{H}_6) = \text{R}^c$.

Again, just as we may consider sulphate of ammonia either as $\text{NH}_4 + \text{SO}_4$, or as $\text{NH}_3, \text{HO} + \text{SO}_3$, so we may view the sulphate of the base b (the oxide of radical b) either as $(\text{PtNH}_3) + \text{SO}_4$, or as $\text{NH}_3, \text{PtO} + \text{SO}_3$, that is, as sulphate of ammonia, in which protoxide of platinum replaces water, or platinum replaces hydrogen.

Further, if we consider the ammoniaco-sulphate of copper to be $2\text{NH}_3 \left. \vphantom{\begin{matrix} \\ \end{matrix}} \right\} + \text{SO}_3$, we may view the sulphate of base a (the oxide of

radical a) as being $2\text{NH}_3 \left. \vphantom{\begin{matrix} \\ \end{matrix}} \right\} \text{PtO} \text{SO}_3$; that is, ammoniaco-sulphate of platinum, platinum replacing the copper of the analogous copper salt. Reiset inclines to this view; but it appears to have no support except from the formulæ, for the ammoniaco-sulphate of copper has no other analogy with the sulphate of base a , and does not, like the latter, yield a caustic alkali when decomposed by baryta.

Enough, however, has been said to show that every view which can be taken of these very interesting compounds connects them with amide, ammonia, and ammonium, for which reason they are here described.

We have entered into considerable detail in regard to these compounds, not only because they are in themselves most remarkable, and because it would have been otherwise impossible to give the student a connected and intelligible account of them, but also because the discovery of these basic compounds throws much light on the origin and constitution of a very important class of compounds, namely, the vegetable bases or alkaloids. All of these contain ammonia or its elements, and there can be little doubt that their basic properties depend on a similarity in constitution to the compounds just described. It is understood that Berzelius has very lately succeeded in demonstra-

ting the true constitution of the organic bases, and his researches are anxiously looked for.

It is necessary to remind the reader, that, while we know the empirical formulæ of the new radicals and bases above described, the rational formulæ above given are only to be regarded as possible arrangements, the chief use of which at present is to aid the student in classifying and retaining the facts, but which he must not permit to influence his judgment in considering the question of their true constitution, any further than is strictly justified by ascertained facts.

There is evidently much to be done before this very interesting subject can be exhausted, and it is hoped that the above view may serve in some measure as a guide to the student should he wish to pursue the investigation for himself. For the details, the reader is referred to the memoirs of Gros, Reiset, and Peyrone in the scientific journals.

When a current of sulphurous acid is passed through a solution of bichloride of platinum, a period arrives when the solution becomes colourless, and gives no precipitate with salammoniac. If now it be supersaturated with carbonate of ammonia, and concentrated, alcohol precipitates a white crystallizable salt. According to Boeckmann, it contains $2\text{SO}_2, 2\text{AdH}, \text{PtO} + \text{HO}$, or $\text{Pt}^{\text{O}}_{\text{Ad}} \} 2\text{SO}_2, \text{AdH}_2\text{O}$. The latter formula contains 1 at. hydrogen less than the former. This compound requires a thorough investigation.

CARBONIC OXIDE.

Formula CO or C_2O_2 .

In certain series of compounds carbonic oxide may be considered as acting the part of a simple substance: viewed in this light, it may be considered as producing, by its combination with oxygen, oxalic acid; with chlorine, phosgene gas; with amide, oxamide; and the croconic and rhodizonic acid may be viewed as a product of the decomposition of its compound with potassium. The compounds of this radical are:—

	Formulæ.	Carbonic Oxide.	Equivalents.
Oxalic Acid	$2\text{CO} + \text{O}$	2 eq. = $28 \cdot 24 + 1$ eq. oxygen = 8	= $36 \cdot 24$.
Chloro-carbonic Acid . .	$\text{CO} + \text{Cl}$	1 eq. = $14 \cdot 12 + 1$ eq. chlor. = 35	$\cdot 42 = 49 \cdot 54$.
Oxamide	$2\text{CO} + \text{NH}_2$	2 eq. = $28 \cdot 24 + 1$ eq. amide = 16	$\cdot 15 = 44 \cdot 39$.
Oxy-carburet of Potassium .	$7\text{CO} + 3\text{K}$	7 eq. = $98 \cdot 84 + 3$ eq. potas. = 117	$\cdot 45 = 216 \cdot 29$.
Rhodizonic Acid . . .	$7\text{CO} + 3\text{HO}$	7 eq. = $98 \cdot 84 + 3$ eq. water = 27	= $125 \cdot 84$.
Croconic Acid	$5\text{CO} + \text{H}$	5 eq. = $70 \cdot 60 + 1$ eq. hydro. = 1	= $71 \cdot 60$.
Mellitic Acid	$4\text{CO} + \text{H}$	4 eq. = $56 \cdot 48 + 1$ eq. hydro. = 1	= $56 \cdot 48$.

OXALIC ACID.

Discovered by Scheele in 1776. It occurs as a mineral humboldite combined with oxide of iron; in several plants, particularly of the

genera oxalis, rumex, &c.; combined with potassa in roots, such as rheum, bistorta, gentiana, saponaria, rumex; with lime, in several kinds of lichens, parmelia cruposa, variolaria, &c. Oxalate of lime is also an ingredient of several urinary calculi; the acid is a product of the decomposition of uric acid, of all organic compounds not containing nitrogen when oxidized by nitric acid, or acted upon by hydrate of potassa (Gay-Lussac), or by permanganic acid (Gregory and Demarçay); it is also formed by the decomposition of cyanogen with water and ammonia.

Prep.—1. By digesting by aid of a gentle heat one part of sugar, or better still of potato starch, in 8 parts of nitric acid of sp. gr. 1.25, as long as gaseous products are evolved; by evaporation the acid is obtained in crystals, which may be purified by a second crystallization after being well dried on paper or porous earthenware. When prepared on a large scale, the process is conducted in cylindrical vessels of earthenware, which are heated by being surrounded with warm water; on a small scale it may be made in a porcelain dish. From 12 parts of potato starch 5 of the acid are obtained. The mother liquor should be treated with an additional quantity of acid, and again warmed, when a second crop of crystals will be obtained; this is repeated until the solution is quite exhausted. On account of the cheapness of nitric acid, this is the only process now adopted in the manufactories. Any nitric acid adhering to the crystals may be removed by gently heating them in a porcelain dish, or by repeated crystallization.

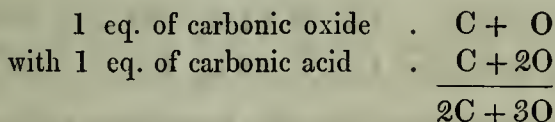
2. By precipitating a solution of the superoxalates of potassa by acetate of lead or sulphuret of barium, carefully washing the precipitate, and decomposing it while yet moist by dilute sulphuric acid. A clear solution is obtained by filtration, which must then be evaporated to crystallization. For the purpose of decomposing the precipitated oxalate of lead or baryta, 5 parts of strong sulphuric acid diluted with 10 of water must be employed for every 7 parts of the binoxalate of potassa. Nine-tenths of the dilute sulphuric acid is to be added in successive portions to the moist lead or barytic precipitate; sulphate of lead or baryta is instantly formed, and the oxalic acid is dissolved by the water. After the mixture has stood some hours, the clear liquid should be poured from the precipitate, which should be repeatedly washed. The solution yields, upon evaporation, crystals of pure oxalic acid; any trace of lead may be removed by sulphuretted hydrogen gas. The residue of sulphate of lead or baryta, which still contains some undecomposed oxalate, must be treated with the remaining tenth of the dilute sulphuric acid, and heated with a little

more water; in this manner an additional quantity of impure oxalic acid is obtained, but the sulphuric acid may be separated from the crystals by washing.

The production of oxalic acid from organic matter is a consequence of the oxidation of the elements of the latter by the oxygen of the nitric acid; hence those substances give it in greatest quantity which contain oxygen and hydrogen in the same proportion as water. In the formation of oxalic acid by permanganate of potassa 1 eq. sugar ($C_{12}H_{10}O_{10}$) and 6 eq. permanganate of potassa give rise to the production of 6 eq. of oxalate of potassa $6(KO, C_2O_3)$, 12 eq. peroxide of manganese ($12MnO_2$), and 10 eq. water ($10HO$). In the double decomposition of oxalate of potassa by sulphuret of barium, sulphuret of potassium, and oxalate of baryta, and in that by acetate of lead, acetate of potassa and oxalate of lead, are formed. The oxalate of baryta or lead is decomposed by sulphuric acid, giving rise to free oxalic acid and sulphates of lead or baryta.

Prop.—The crystallized oxalic acid is a compound of the hydrate with water of crystallization; it forms colourless transparent oblique rhombic prisms, with one or two terminal planes; one pair of the lateral edges of the latter is sometimes truncated, giving rise to an irregular hexagonal prism, acuminate by 2 or 4 planes; their sp. gr. = 1.507. It is without odour, tastes and reacts strongly acid, and is poisonous. The antidote is chalk or magnesia. The crystals when heated fall into a powder, and lose 28 per cent. = 2 eq. of water of crystallization; the hydrate of oxalic acid is left. When rapidly heated to the temperature of 350° they fuse and lose their water of crystallization, a part of them decomposing, while another portion sublimes as hydrate in dense white fumes of a strong odour, which cover the surface of the fused acid in the form of a woolly crystalline mass. If heated in a retort to 310° , it is completely decomposed into carbonic oxide, carbonic acid, and formic acid, without leaving any residue.

When heated in strong sulphuric acid, it is entirely decomposed into carbonic acid, carbonic oxide, and water. The anhydrous oxalic acid may be considered as a compound of



which accounts for the production of equal volumes of carbonic oxide and carbonic acid, whenever the pure acid or any of its salts is heated in strong sulphuric acid. This decomposition is not attended with the blackening of the acid, or the evolution of any other gas; it fur-

nishes an important means of recognizing and distinguishing the oxalic acid and its combinations from any other substance. When heated with peroxide of manganese or other superoxides, these are reduced to protoxides, which unite with one portion of the oxalic acid, while another portion of it is converted into carbonic acid by the oxygen liberated.

The volume of carbonic acid formed may be used to determine the quantity of oxygen in these oxides.

The crystals dissolve in 8 parts of water at 60° , in their own weight of boiling water, and in 4 parts of alcohol at 60° .

When pure, the oxalic acid is colourless, has no corrosive action on paper, and is not deliquescent: the precipitate, which is formed by salts of baryta, is perfectly soluble in nitric acid; if it contain lead, it is blackened by sulphuretted hydrogen; it should sublime without leaving a residue.

The oxalic acid and its soluble salts are in analytical chemistry the most important reagent for the detection and separation of lime.

In the neutral salts of oxalic acid, the oxygen of the base is to that of the anhydrous acid in the proportion of 1 : 3. If the oxygen of the metallic oxide be considered as a part of the acid, the compound contains carbonic acid and a metal. Many salts of oxalic acid, whose bases are oxides easily reduced to the metallic state, are decomposed by heat into carbonic acid and metal. Thus, the oxalates of nickel and cobalt, when heated in close vessels, yield carbonic acid and pure nickel or cobalt; oxalate of silver is reduced with a slight explosion. The oxalates of the alkalis under the same circumstances evolve carbonic oxide, and are converted into carbonates. Many metallic oxides when heated with an oxalate are reduced by the carbonic oxide gas evolved. All salts of oxalic acid evolve carbonic oxide and carbonic acid gases, when heated in strong sulphuric acid, without being blackened; there exist both neutral and acid salts; the latter contain double, and sometimes four times as much acid as the former.

Formula, $2\text{CO} + \text{O}$ or C_2O_3 ; symb. $\overline{\text{O}}$; eq. = 36.24 . Dulong, Berzelius.

Of the hydrate . 1 at. $\overline{\text{O}} + 1$ eq. HO eq. = 45.24 .

Of the crystallized 1 at. $\overline{\text{O}} + 3$ eq. HO eq. = 63.24 .

Oxalate of Ammonia.—*Prep.*—By neutralizing a solution of pure oxalic acid by caustic or carbonate of ammonia, or by decomposing the oxalate of lead by sulphuret of ammonium, and evaporating the solution to crystallization. It may also be prepared by neutralizing the bin- or quadroxalate of potassa with carbonate of ammonia; the first crop of crystals consists of oxalate of ammonia, which may be com-

pletely freed from potassa by repeated crystallization; the mother liquor contains the neutral oxalate of potassa.

Prop.—Crystallizes in long colourless and transparent prisms of the right prismatic system; of a strong saline taste; is less soluble than the oxalic acid; effloresces in a warm atmosphere, losing 12·6 per cent. of water of crystallization. Is used for the purpose of separating lime from magnesia, and generally for precipitating lime from its solutions. By heat it is decomposed, giving rise to two very remarkable products, oxamide and oxamic acid. When a solution of this salt containing chloride of potassium is evaporated to dryness, and the residue is heated to redness, sal-ammoniac is evolved and a part of the potassium remains in the state of carbonate.

Its formula is $\text{NH}_4\text{O}, \text{C}_2\text{O}_3 + \text{aq.}$ in crystals.

The binoxalate of ammonia $\text{NH}_4\text{O}, 2\text{C}_2\text{O}_3 + 2 \text{ aq.}$ is less soluble than the neutral salt. There is also a quadroxalate of ammonia, composed of 4 eq. of oxalic acid, 1 eq. of oxide of ammonium, and 3 eq. of water. (Graham.)

Oxalate of Potassa.—*Prep.*—By neutralizing the acid salts of commerce, or the pure oxalic acid, by carbonate of potassa, and evaporating to crystallization. By fusing organic matter, as paper, tartaric acid, &c., with hydrate of potassa.

Prop.—Crystallizes in colourless transparent rhombic prisms; is permanent in the air; heated to 160° becomes opaque, and loses 9·7 per cent. = 1 eq. of water, has a cooling bitter taste, is soluble in 3 parts of water, is insoluble in alcohol.

The formula of the crystals is $\text{KO}, \text{C}_2\text{O}_3 + \text{aq.}$ (Graham);* eq. = 92·39.

Binoxalate of Potassa.—*Prep.*—By neutralizing one part of crystallized oxalic acid by carbonate of potassa, and afterwards adding to the neutral salt another part of oxalic acid, and crystallizing. It was formerly procured by expressing the juice of the oxalis acetocella, clarifying by white of egg or milk, and evaporating to crystallization.

Prop.—Crystallizes in transparent, colourless, oblique rhombic prisms, tastes and reacts strongly acid, is poisonous, is dissolved by 40 parts of cold, and 6 parts of boiling water; is insoluble in alcohol.

When pure, this salt, if heated, should fuse and decompose without emitting a burnt odour, and the residue should be of a grey not a black colour. The presence of cream of tartar is recognized by the carbonaceous residue, and the peculiar odour which it emits on burning; of sulphate of potassa, by the common tests for sulphuric acid. If of two equal parts by weight of the salt, the one be exposed to a

* The names placed behind the formulæ denote the chemists from whose analyses they are taken.

red heat, and the other be dissolved in water, the solution of the latter should be deprived of its acid reaction by the addition of the residue of the former; if this does not happen, it is not the binoxalate, but the following salt, which is the only one at present sold in commerce under that name.

It is used and sold as the essential salt of lemons, for removing iron-moulds and other metallic stains (ink, &c.); the following salt may be employed for the same purpose.

The formula of the crystals is $\left\{ \begin{array}{l} \text{HO, C}_2\text{O}_3 \\ \text{KO, C}_2\text{O}_3 \end{array} \right\} + 2 \text{ aq.}; \text{ eq.} = 155.63.$
(Graham.)

Quadroxalate of Potassa.—Is sold in commerce as binoxalate. It is procured by dissolving the binoxalate in hydrochloric acid, and crystallizing; it is made on the large scale by neutralizing one part of crystallized oxalic acid, and adding to the solution three parts of the pure acid.

Prop.—It crystallizes in colourless transparent prisms of the doubly oblique prismatic system; is as insoluble in water as the binoxalate; loses at 262° two atoms, or 14 per cent. of water; at higher temperatures oxalic acid volatilizes with decomposition. If pure, its reaction, when heated, is similar to that of the binoxalate; if three parts of the salt be converted into carbonate by a red heat, and added to a solution of one part, the neutral oxalate of potassa should be obtained.

Its crystals are $\left\{ \begin{array}{l} \text{KO, C}_2\text{O}_3 \\ 3(\text{HO, C}_2\text{O}_3) \end{array} \right\} + 4 \text{ aq.}; \text{ eq.} = 264.11$ $\left\{ \begin{array}{l} \text{Berzelius.} \\ \text{Graham.} \end{array} \right.$

Oxalate of Soda.—The most insoluble of the soda salts; is with difficulty obtained in distinct crystals, and is always anhydrous; there is a bin-, but no quadroxalate of soda.

Its symbol is $\text{NaO, C}_2\text{O}_3$; $\text{eq.} = 67.54.$

Oxalate of Lime.—*Prep.*—Occurs in several species of lichen, of which it forms the firm hard skeleton, so that many of them, namely the *variolaria communis* (*porophora pertusa*) may be used for preparing oxalic acid, but not very advantageously. The pounded lichens should, according to Braconnot, be mixed with one-third their weight of concentrated sulphuric acid, which is diluted with its own weight of water, and the whole boiled for half an hour, separated from the gypsum while boiling hot, and the clear solution evaporated to crystallization. The crystals contain lime, and can only be used for preparing the soluble salts of oxalic acid.

The insolubility of the oxalate of lime in water, ammonia, and acetic acid, and its solubility in the nitric and hydrochloric acids, distinguishes it characteristically from most other precipitates. Advan-

tage is taken of this to detect lime in solutions from which all other precipitable metallic oxides have been separated by other means, the alkaline oxalates being the best reagents for this purpose; thus these oxalates are used to separate lime from magnesia, with the latter of which they form soluble double salts. On the other hand, lime may be used to detect oxalic acid; but it must here be remembered that oxalic acid is imperfectly precipitated by salts of lime from a solution which contains the oxides of chromium, iron, or manganese.

Recently precipitated oxalate of lime is a snow-white flocculent powder, insoluble in acetic acid, readily dissolved by free nitric or hydrochloric acid, and by a red heat is converted without being perceptibly blackened into carbonate of lime, from the weight of which, either the oxalic acid or the lime may be calculated.

Symb. $\text{CaO}, \text{C}_2\text{O}_3 + 2 \text{ aq.}$; $\text{eq.} = 82.74$. (Graham.)

Oxalate of magnesia, of oxide of zinc and protoxide of manganese, are analogous in their composition with the salt of lime.

Oxalate of baryta is $\text{BaO}, \text{C}_2\text{O}_3 + \text{aq.}$ (Graham.)

Oxalate of Chromium and Potassa.—Discovered by W. Turner, and by Gregory about the same time. Obtained by dissolving by the aid of heat one part of bichromate of potassa, two of the binoxalate of potassa, and two of oxalic acid, and evaporating to crystallize. The solution is accompanied by the rapid evolution of carbonic acid, which is derived from the mutual decomposition of the oxalic and chromic acids, a part of the former being converted into carbonic acid by depriving the latter of half its oxygen. The crystals of the salt are black by reflected, deep blue by transmitted light; the solution green by reflected, and red by transmitted light. Alkalies throw down only a part of the oxide of chromium, and salts of lime produce a very slight precipitate.*

Its symb. is $\text{Cr}_2\text{O}_3, 3\text{C}_2\text{O}_3 + 3(\text{KO}, \text{C}_2\text{O}_3) + 6 \text{ aq.}$ (Graham.)

Chloro-carbonic Acid.—Discovered by J. Davy, and called by him phosgene. Prepared by exposing equal measures of dry chlorine and carbonic oxide gases to sunshine, when combination ensues in the course of a few minutes, and they contract to half their volume. Diffused daylight causes their union in some hours; but they do not combine at all when the mixture is wholly excluded from light.

Prop.—A colourless gas, has a strong disagreeable odour, excites a flow of tears, and is soluble in water, by which it is decomposed, giving rise to the formation of carbonic and hydrochloric acids. Many metals, when heated in this gas, combine with its chlorine, and liberate

* For an account of the remarkable optical properties of this salt, the reader is referred to a paper by Sir David Brewster in the *Edin. Phil. Trans.*

the carbonic oxide; several oxides effect the same change, but with the formation of carbonic acid. With alcohol it suffers a very peculiar decomposition; it combines with ammonia, forming a white crystalline solid, which is volatile, and may be sublimed without change, is deliquescent, and is very soluble in water; its symbol is $2\text{NH}_3 + \text{COCl}$.

Its symb. is COCl ; eq. = 49.54. It may be viewed as carbonic acid, in which one-half of the oxygen has been replaced by chlorine.

OXAMIDE.

The nature of this substance was first developed by Dumas, but it was first obtained by Bauhof by the action of oxalic acid on alcohol. It is formed by the distillation of oxalates with ammoniacal salts, or of oxalate of ammonia; of the greatest purity, by decomposing oxalic ether by an excess of a solution of ammonia.

Prop.—A snow-white crystalline powder, void of taste or smell; almost insoluble in alcohol, ether, and cold water, but taken up in small quantity by boiling water; unchanged by dilute, but by concentrated acids or alkalies readily converted with the aid of heat into oxalic acid and ammonia. By the destructive distillation it is decomposed into water, carbonic oxide, hydrocyanic acid, cyanic acid, and ammonia, the two last of which combine and form urea.

If the composition of oxamide be compared with that of oxalate of ammonia, the explanation of its origin and its decomposition will at once be seen.

Oxalate of ammonia is $\text{NH}_3\text{C}_2\text{O}_3 + 2 \text{ aq.}$, subtract the constituents of oxamide

There is left . $\text{H} \quad \text{O} + 2 \text{ aq.}$

Oxamide is formed therefore by the separation of one equivalent of water from the constituents of anhydrous oxalate of ammonia. The oxalic ether is a compound of anhydrous oxalic acid with ether: this compound is instantly decomposed by a solution of ammonia; the oxalic acid gives 1 eq. of oxygen to 1 eq. of hydrogen of the ammonia, forming water, which produces alcohol by uniting with the ether; while, on the one hand, carbonic oxide C_2O_2 , and on the other amide NH_2 is liberated, and these by combining give rise to the formation of oxamide. $(\text{C}_4\text{H}_5\text{O}, \text{C}_2\text{O}_3) + \text{NH}_3 = \text{NH}_2, \text{C}_2\text{O}_2 + (\text{C}_4\text{H}_5\text{O} + \text{HO.})$

When oxamide is heated in contact with alkalies, which are capable of uniting with oxalic acid, or with acids which will combine with ammonia, 1 eq. of water is added to its constituents, and it decomposes

into oxalic acid and ammonia. The same thing occurs when oxamide and water are exposed to a temperature exceeding 212° under a high pressure. The manner in which oxamide is decomposed by acids is highly interesting, as it appears to throw some light upon certain changes which many organic substances, namely, starch and wood, undergo, by exposure to the action of dilute or concentrated mineral acids, when a certain quantity of water enters into their constitution, and they are converted into sugar. A very small quantity of oxalic acid, for example, will suffice to convert an unlimited quantity of oxamide into neutral oxalate of ammonia, and the oxalic acid, after effecting the change, remains unaltered in the solution; were the new product (oxalate of ammonia) not decomposed by alkalies into its constituents, this decomposition would be exactly similar to the conversion of starch into sugar, and those chemists who suppose the existence of the catalytic force, would be under the necessity of attributing the decomposition of oxamide to that power.

Its symb. is $\text{NH}_2 + \text{C}_2\text{O}_2$; eq. = 44.39.

Oxamide is interesting as being the type of a numerous class of compounds, all of which are equivalent to salts of ammonia with acids, *minus* the elements of water, and, like oxamide, are reconverted into ammonia and acids by boiling with strong acids or alkalies. These compounds are distinguished by the termination *amide*, implying that they are formed of amide united to the acid, *minus* oxygen. Thus we have benzamide, succinamide, asparamide, &c.

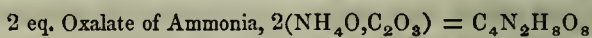
But oxamide is not the only product of the action of heat on oxalate of ammonia, for besides carbonic acid, carbonic oxide, water, hydrocyanic acid, ammonia, and oxamide, all of which may be formed, according to the heat employed, Balard has shewn that there is produced, when the heat is carefully regulated so that only water and ammonia are expelled, and a honey yellow residue left in the retort, a new acid, called oxamic acid, which is, however, contaminated with a little oxamide. Hot water dissolves the acid alone, and it is easily purified. When dissolved in ammonia, with which it forms a very soluble salt, it is precipitated by acids from the concentrated solution as a white powder, sparingly soluble in water, the formula of which is $\text{C}_4\text{H}_2\text{NO}_5 + \text{HO}$. It forms soluble salts with lime, baryta, and oxide of silver.

This compound, although an acid, may yet be viewed as a compound of amide—as an acid amidide $\text{NH}_2 + \text{C}_4\text{O}_5$. In accordance with this view, it is resolved when boiled with alkalies into oxalic acid and ammonia $\text{NH}_2, \text{C}_4\text{O}_5 + 3\text{HO} = (\text{NH}_4\text{O}, \text{C}_2\text{O}_3) + (\text{HO}, \text{C}_2\text{O}_3)$. Here, 3 eq. of water being taken up, binoxalate of ammonia is the result; and this serves to distinguish oxamic acid from oxamide, which, under

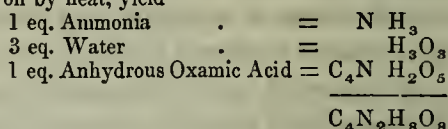
similar circumstances, takes up 2 eq. of water, and yields the neutral oxalate.

A few acid amidides are known, and one will be described a little further on, derived from mellitate of ammonia, which is called euchronic acid, and, like oxamic acid, is accompanied by a neutral amidide, in this case paramide.

The production of oxamic acid is easily explained; for



when acted on by heat, yield



Berzelius considers oxamic acid as a coupled oxalic acid, in which the adjunct body is oxamide, for $\text{C}_4\text{H}_2\text{NO}_5 = \text{C}_2\text{O}_3 + (\text{C}_2\text{O}_2\text{NH}_2)$.

When to an alcoholic solution of oxalic ether there is added just so much ammonia that a precipitate of oxamide begins to appear, the liquid, by evaporation, now yields beautiful pearly tabular crystals of a body formerly called oxamethane, which, however, appears to be oxamate of oxide of ethyle. Its formula is $\text{C}_8\text{NH}_7\text{O}_6 = (\text{C}_4\text{H}_5\text{O}) + (\text{C}_4\text{NH}_2\text{O}_5)$.

RHODIZONIC ACID.

Discovered by L. Gmelin. When a stream of dry carbonic oxide gas is transmitted over a portion of fused potassium, the gas is absorbed in large quantities; the potassium coats the surface of the glass tube, becomes green, and at last a black porous mass is obtained, which, if exposed to the air when warm, inflames, and if covered with water dissolves with the rapid evolution of a combustible gas; if moistened with water it burns, and forms a red solution which contains rhodizionate of potassa. This compound of potassium and carbonic oxide is obtained in considerable quantity as a secondary product during the preparation of potassium, when it separates from the gases evolved in the form of a grey powder, which may readily be collected. Exposed to a moist air it slowly absorbs oxygen, and is converted, without combustion, into rhodizionate of potassa of a scarlet colour; by being treated with alcohol, in which it is insoluble, the free potassa may be separated.

The researches of Heller prove that this potassa salt contains a peculiar acid, the composition of which, according to the analysis of Thaulow, may be represented by the formula $\text{C}_7\text{H}_3\text{O}_{10}$, or $\text{C}_7\text{O}_7 + 3 \text{ aq.}$, the potassa being supposed to be replaced by water; consequently of

carbon and oxygen in the same proportion as in 7 eq. of carbonic oxide united with 3 eq. of water. The potassa salt is represented by the formula $C_7O_7 + 3KO$, the lead salt by $C_7O_7 + 3PbO$. The acid is decomposed when an attempt is made to separate it from the oxide of lead by sulphuretted hydrogen; it is obtained mixed with sulphovinate of potassa, when its salt of potassa is decomposed by a mixture of sulphuric acid and alcohol; all its compounds are of a red colour, or, in the dry state, of a brilliant metallic green.

The changes which are produced on rhodizionate of potassa when its aqueous solution is heated are very remarkable; without the evolution of gases it is decomposed into free potassa, oxalate of potassa, and into the potassa salt of a new acid, which has been called the croconic acid by its discoverer L. Gmelin.

Croconic Acid.—If the yellowish-red solution of rhodizonic acid be heated, it acquires a lemon-yellow tint, and deposits, on evaporation, brilliant acicular crystals of a yellow colour; the alkaline solution yields at last oxalate of potassa.

The croconic acid is prepared by adding hydrofluosilicic acid to a solution of its potassa salt, and evaporating to dryness; the pure acid is removed from the yellow residue by water; it is yellow, readily crystallized, tastes and reacts strongly acid, is soluble in water and alcohol; all its salts are yellow, and, with the exception of the ammoniacal salts, are all of them insoluble in alcohol.

The hypothetical anhydrous acid is C_5O_4 ; the probable composition of the hydrate C_5O_5H .

Croconate of Potassa.—Crystallizes in long six-sided prisms of an orange-yellow colour, and tastes similar to nitre; is neutral with respect to vegetable colours, loses when gently heated 15 per cent. = 2 eq. of water, and acquires a lemon-yellow colour; if heated, burns like tinder into a mixture of carbonate of potassa and carbon, without emitting any burnt odour, but accompanied by the evolution of carbonic oxide and carbonic acid gases; it is decomposed by chlorine and nitric acid with gentle effervescence into peculiar crystalline salts, which have not yet been studied.

The compound of potassium with carbonic oxide contains no rhodizonic acid; the latter is first produced when the former is added to water. The development of gases rich in hydrogen proves that the potassium is not present in an oxidized state. If the constitution of the potassium compound be represented by the formula $C_7O_7 + 3K$, the rhodizionate of potassa may be considered as formed by the decomposition of three atoms of water. The decompositions do not appear, however, to be quite so simple, for, according to the experiments of

E. Davy, the gas evolved is not pure hydrogen, but a new substance, which is distinguished from all known gases by being spontaneously combustible at common temperatures when mixed with chlorine, with the deposition of carbon. Rhodizionate of potassa contains the elements of 1 eq. of oxalate of potassa $\text{KO}, \text{C}_2\text{O}_3$, 1 eq. of croconate of potassa $\text{C}_5\text{O}_4, \text{KO}$, and one of free potassa KO , which sufficiently explains its decomposition.

Croconic acid may be considered as a compound of carbonic oxide and hydrogen $\text{C}_5\text{O}_5 + \text{H}$, and stands in this point of view in very close relation with another remarkable acid, namely, the mellitic, which in all its combinations behaves as a compound of a similar radical with hydrogen.

Mellitic Acid.—Discovered by Klaproth. In combination with alumina constitutes a very rare mineral, the honey-stone. Best prepared, according to Wöhler, by decomposing the mellitate of lead by sulphuretted hydrogen. The solution separated by filtration from the sulphuret of lead yields, on evaporation, a white slightly crystalline powder; it is soluble in alcohol, from which it may be obtained by very slow evaporation in radiated groups of acicular crystals. The aqueous solution tastes and reacts strongly acid. The dry mellitic acid is not changed by boiling in nitric or sulphuric acid; boiled in alcohol, it seems to form an acid mellitate of ether. It forms salts by uniting with the base; its alkaline salts are soluble, and may be obtained in crystals, but with the other metallic oxides it forms either insoluble, or very sparingly soluble, compounds. Their general formula when dried at 212° is $\text{MO} + \text{C}_4\text{O}_4\text{H}$. When heated they are decomposed, but the silver salt suffers in the first instance a peculiar change; at the temperature of 356° one equivalent of water is separated, and its composition is then $\text{C}_4\text{O}_4\text{Ag}$. Since the silver salt dried at 212° can retain no water, it is exceedingly probable that the water is first formed at the above heat by the hydrogen of the acid, and the oxygen of the oxide of silver, when the salt passes into a combination of silver and carbonic oxide C_4O_4 , the latter acting the part of chlorine or any other haloid substance. By hydrosulphuric or hydrochloric acid, unaltered mellitic acid may be obtained from the salt thus heated.

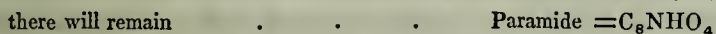
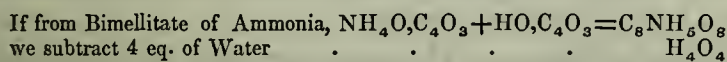
The silver salt dried at 356° may also be considered as a compound of oxide of silver AgO , with an acid C_4O_3 , which differs from oxalic acid by containing a double quantity of carbon.

Formula $\text{C}_4\text{O}_4 + \text{H}$; eq. = 57.48.

Mellitate of Ammonia.—Prepared by digesting honey-stone in carbonate of ammonia, when a solution of the salt is obtained and alumina deposited. It crystallizes in two forms, arising probably from dif-

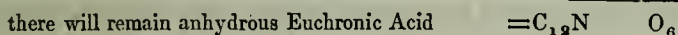
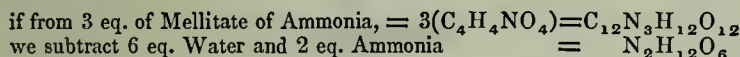
ferent quantities of water; they both belong to the right rhombic system; the crystals are large, brilliant, and transparent; in the air they become opaque and milk-white. When this salt $\text{NH}_3\text{HO}, \text{C}_4\text{O}_3 = \text{C}_4\text{NH}_4\text{O}_4$, is heated to 320° , it gives off ammonia and water, and there remains a mixture of two new compounds: a soluble one, which contains *euchronic acid* in combination with ammonia; and an insoluble one, which is called *paramide*.

Paramide is a yellow solid, like clay. Its most remarkable character is that, when long boiled with water, it is converted into bimellitate of ammonia. This is the character of an amide, hence its name. The composition of paramide is C_8HNO_4 , which readily explains both its formation, and its conversion into bimellitate of ammonia.

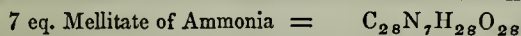
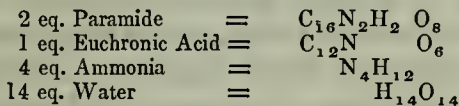


and of course, when reconverted into bimellitate of ammonia by long boiling, it merely takes up again these 4 eq. of water.

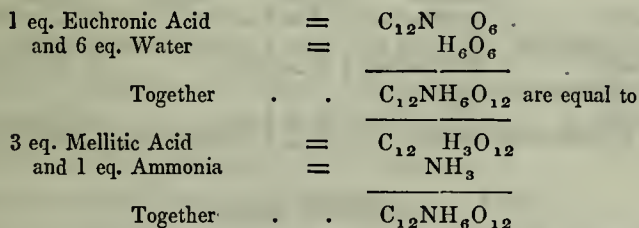
The soluble compound, euchronate of ammonia, when its solution is acted on by hydrochloric acid, deposits a white crystalline powder, which is euchronic acid, $\text{C}_{12}\text{NO}_6, 2\text{HO}$. Its formation is easily explained; for



We can now see that the action of heat on 7 eq. of mellitate of ammonia gives rise to the following substances:—



When euchronic acid is boiled with water, it is dissolved and converted into an acid mellitate of ammonia.



Euchronic acid is deoxidized by a plate of zinc, yielding a powder of a fine deep blue colour, which dissolves in ammonia or potash, with

a splendid tint of purple. The blue powder is an inferior oxide of the same nitrogenised radical, which, combined with more oxygen, forms euchronic acid. The whole subject of mellitic acid and euchronic acid is most interesting, but mellitic acid is so rare that it is very difficult to find material for the investigation. As mellitic acid, like succinic acid, is of organic origin, and contains only 1 eq. of hydrogen less, and 1 eq. of oxygen more than succinic acid, we may hope to be enabled to obtain it artificially.

Its formula is $\text{NH}_3 + \text{C}_4\text{O}_4\text{H}$.

Mellitate of Lead is formed by adding mellitic acid to acetate of lead, or by mixing the mellitate of ammonia with any salt of lead; a voluminous white precipitate is formed, which, when washed and dried, becomes a heavy crystalline powder.

Mellitate of Alumina.—The native crystals, the honey-stone of mineralogists, is found in a stratum of brown coal in Saxony, in transparent yellow octohedrons: they are insoluble in cold; but decomposed by hot water, contain 14·5 per cent. of alumina, 41·4 of mellitic acid, and 44·1 of water (Wöhler); therefore 3 eq. of acid, 1 eq. of alumina, and 18 eq. of water.

CARBON AND NITROGEN.

CYANOGEN.

Cyanogen unites as a compound radical with oxygen, hydrogen, and most other non-metallic elements, and also with the metals; many of the latter compounds are similar to the haloid salts, but others, on the contrary, possess a perfectly different character. The discovery of cyanogen and its chemical nature, due to Gay-Lussac, has proved of the highest importance for organic chemistry. Cyanogen is composed of 2 eq. of carbon and 1 eq. of nitrogen; its formula is C_2N ; symb. Cy; eq. = 26·39.

CYANOGEN AND OXYGEN.

	Cyanogen.	Oxygen.	Water.	Equiv.	Formulae.
Cyanic Acid . . .	26·39=1 eq.	+ 8 = 1 eq.		= 34·39	CyO .
Hydrated Cyanic Acid	26·39=1 eq.	+ 8 = 1 eq.	+ 9=1 eq.	= 43·39	$\text{CyO} + \text{HO}$.
Fulminic Acid . . .	52·78=2 eq.	+ 16 = 2 eq.		= 68·78	Cy_2O_2 .
Hydrated Fulminic Acid	unknown.				
Cyanuric Acid . . .	79·17=3 eq.	+ 24 = 3 eq.		= 103·17	Cy_3O_3 .
Hydrated Cyanuric Acid	79·17=3 eq.	+ 24 = 3 eq.	+ 27=3 eq.	= 130·17	$\text{Cy}_3\text{O}_3, 3\text{HO}$.

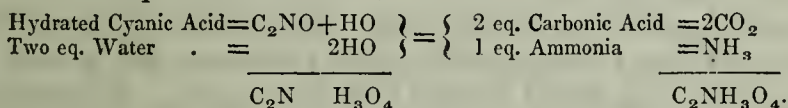
CYANIC ACID.

Hist.—Discovered by Wöhler. Is formed when cyanogen is transmitted over carbonate of potassa at a red heat, or into an alkaline solu-

tion; by exposing compounds of cyanogen at a red heat to the action of the air, of nitre, or of peroxide of manganese; by fusing ammeline, melamin, or ammeline with hydrate of potassa; and by adding oxide of lead to fused cyanide of potassium, as prepared by Liebig's process. It is a frequent product of the decomposition of compounds of nitrogen. It is not known in the anhydrous state.

Prep.—As hydrate, by distilling dry cyanuric acid or cyamelide in a retort, when they are converted into hydrate of cyanic acid, which must be collected in a receiver well cooled by ice. Here 1 eq. of cyanuric acid $Cy_3O_3, 3HO$ is resolved, without change of weight into 3 eq. cyanic acid, $3(CyO, HO)$. Cyamelide is also isomeric or polymeric with cyanic acid, and a similar explanation applies.

Prop.—A clear transparent fluid of a strong penetrating odour, similar to that of acetic or formic acid, exceedingly volatile, and causing blisters on the skin, which are accompanied by great pain. Mixes readily with water. Decomposes with the production of great heat shortly after its formation into a white solid of the same composition per cent. (cyamelide); its aqueous solution reddens vegetable colours strongly; it decomposes in the course of a few minutes, together with two equivalents of water, into bicarbonate of ammonia:



This decomposition with water is the cause of the impossibility of obtaining the free acid from the aqueous solutions of its salts by the action of a stronger acid, although a small quantity, as may readily be recognized by the peculiar odour which accompanies the carbonic acid evolved, does escape decomposition.

The cyanic acid forms only one series of salts with the bases; they are readily recognized by the peculiar decomposition produced by dilute mineral acids. A few moments after mixing the salt with the acid, a rapid effervescence, accompanied by a strong penetrating odour of cyanic acid, is observed, and the solution by being mixed with hydrate of lime evolves ammonia abundantly, which previous to the decomposition cannot be detected. Its salts with the alkaline bases and with ammonia are soluble, the others are insoluble; the former, with the exception of the ammoniacal salt, are decomposed, when their solutions are boiled, into ammonia and carbonates.

Its formula is $CyO, HO = C_2NO, HO$; eq. = 43.39.

Cyanates of Ammonia.—Cyanic acid forms with ammonia two compounds, one of which is particularly remarkable from its identity with urea.

1. *Basic Cyanate of Ammonia*.—When dry ammoniacal gas and the vapour of hydrated cyanic acid are simultaneously conducted into a dry vessel, they unite, forming a white woolly crystalline compound, which contains more ammonia than corresponds to the constitution of a neutral cyanate. It is similar in all its properties to any other salt of cyanic acid; treated with an acid it is decomposed with effervescence, and alkalies effect the evolution of ammonia; but if on the contrary it be gently warmed, whether dry or in solution, or if it be left for some time exposed to the air, ammonia is given off, it loses all the above mentioned properties, and is converted into urea.

2. *Anomalous Cyanate of Ammonia; Urea*.—Discovered by Fourcroy and Vauquelin in urine, by Wöhler as the first organic compound artificially produced. It is a constituent of uric acid, and is contained in the urine in combination with lactic acid (Henry). Urea is also a product of the reaction of cyanogen on water when a solution of that gas is allowed to undergo spontaneous decomposition (Pelouze and Richardson).

Prep.—By mixing fresh urine evaporated to the consistence of a syrup at a gentle heat, which should never reach that of ebullition, when still warm, with its own volume of colourless nitric acid of sp. gr. = 1.42. If the evaporation has been carried sufficiently far, the whole will form a thick crystalline mass; to ensure this, a small portion of the urine should be tried from time to time. The crystalline mass consists of a compound of nitric acid and urea, which is sparingly soluble in nitric acid. By the action of the nitric acid on the warm solution heat is developed, and effervescence ensues. This is chiefly owing to the destruction of the colouring matter, and if no external heat is applied, the urea not only is not decomposed, but forms, from the first, nearly white crystals of nitrate. When cold is employed, according to the method formerly recommended, the crystals are very brown, and are purified with difficulty. It is advisable to separate from the inspissated urine as much as possible of the chlorides it contains, by crystallization, before adding the nitric acid (Cap and Henry).

A solution of the colourless crystals of the nitrate of urea is treated with carbonate of baryta until it is rendered perfectly neutral; on evaporating, crystals of nitrate of baryta, and then of urea, will be obtained. The crystals of the latter, by being re-dissolved in a little cold water, are freed from the last portions of the nitrate of baryta; the solution in alcohol gives crystals of pure urea (Wöhler). Gregory states that coloured crystals of urea are best decolorized by a little permanganate of potash, which destroys the colouring matter, but has

no action on urea. Any excess of the salt is removed by alcohol, which converts it into peroxide of manganese.

Instead of using nitric acid, the concentrated urine may be added to a boiling saturated solution of oxalic acid, when the sparingly soluble oxalate of urea falls, which, after being deprived of its colour by charcoal, may be decomposed into the insoluble oxalate of lime and pure urea, by being digested with pounded chalk (Berzelius).

But by far the best method of obtaining urea is to form it artificially, as recommended by Liebig. 28 parts of dried ferrocyanide of potassium, and 14 of peroxide of manganese are mixed in powder and calcined, as above described, on a flat iron plate at a very low red heat, sufficient to keep up the glow which takes place. When this is over, the cold mass, powdered, is acted on by a moderate quantity of cold water, which dissolves the cyanate of potash. This is filtered off, and set aside. A fresh portion of cold water being added to the powder, to wash it, is also filtered, and in this liquid are now dissolved $20\frac{1}{2}$ parts of sulphate of ammonia, and the solution is added to the first filtered solution of the cyanate. A large quantity of sulphate of potash is deposited, which is strained off, and the filtered liquid now containing, with some sulphate of potash, all the cyanate of ammonia, is evaporated to dryness, during which process the cyanate of ammonia is transformed into urea. The dry mass is digested in alcohol, which dissolves only the urea, and yields it from the first chemically pure and in any quantity, if the operation be carefully performed. Urea thus obtained is far cheaper than that extracted from urine.

Prop.—Crystallizes in colourless, transparent, four-sided, somewhat flattened prisms of the sp. gr. 1.35, is soluble in its own weight of cold, and in every proportion in hot water, in 4.5 parts of cold, and in 2 parts of boiling alcohol: the aqueous solution has a cooling bitter taste like nitre; when pure it is perfectly permanent in the air, is not deliquescent, fuses at 250° into a colourless liquid, is decomposed by a higher temperature into ammonia, cyanate of ammonia, and dry solid cyanuric acid. Alkalies do not cause the separation of ammonia in the cold. Urea is an organic base, and unites with several acids without decomposition to crystallizable saline compounds: by evaporating its solution with nitrate of silver or acetate of lead it is decomposed; the products being, with the first, nitrate of ammonia and crystalline cyanate of silver; with the second, acetate of ammonia and carbonate of lead. With hypo-nitrous acid it is instantly decomposed into ammonia, water, and nitrogen and carbonic acid gases, which are evolved in equal volumes; $C_2N_2H_4O_2 + NO_3 = NH_3 + HO + 2CO_2 + N_2$. With 2 eq. of hyponitrous acid, it might be entirely resolved into

water, carbonic acid and nitrogen; $C_2N_2H_4O_2 + 2NO_3 = 4HO + 2CO_2 + N_3$; but in this case there would be 3 vols. of nitrogen to 2 of carbonic acid; with chlorine it forms hydrochloric acid, nitrogen, and carbonic acid. When fused with the hydrated alkalies, or heated in concentrated sulphuric acid, it is decomposed together with the constituents of 3 eq. of water into carbonic acid and ammonia. Urea contains the elements of cyanate of ammonia ($NH_4O + C_2NO$); it may also be considered, according to Dumas, as a second compound of carbonic oxide and amide, in which the quantity of the latter is double that in oxamide $C_2O_2 + 2NH_2$.

Nitrate of Urea.—This compound, when recently precipitated from urine, appears in the form of fine crystalline plates of a brown colour and mother-of-pearl lustre; the purer they are, the more they lose this appearance: a solution of pure urea treated with nitric acid gives a granular white crystalline precipitate, which is soluble in 8 parts of cold, but more freely in hot water, from which it crystallizes in broad, scarcely translucent plates; is sparingly soluble in nitric acid, with which it may be boiled without decomposition. Is composed of 1 eq. of nitric acid, 1 of urea, and 1 of water (Regnault).

Oxalate of Urea forms long transparent prisms, and is, as formerly stated, even more sparingly soluble than the nitrate.

Acetate of Urea.—I have obtained this salt in long prisms, very soluble in water.

Cyanate of Potassa.—*Prep.*—By roasting at a red heat dry ferrocyanide of potassium in fine powder upon an iron plate, the powder being constantly stirred; the cyanide of potassium contained in the salt is thus converted, by absorbing the oxygen of the air, into cyanate of potassa. As soon as it is baked into one mass, owing to the fusion of the cyanate of potassa forming, it must be reduced to a fine powder and digested in boiling alcohol, from which, as the solution cools, crystals of the cyanate are deposited. A mixture of two parts of ferrocyanide of potassium, and one of peroxide of manganese, may be treated in the same way. This mixture may be kindled by a red-hot body, when it smoulders away into a brown mass which contains cyanate of potassa, carbonate of potassa, and sesquioxide of manganese. This salt may also be procured of great purity, but not so economically, by fusing the hydrate of potassa in a silver vessel, and adding melam, ammeline, or amelide in successive portions as long as they are dissolved; the fused transparent mass congeals, on cooling, to a pure crystalline cyanate of potassa.

Prop.—Crystallizes from the alcoholic solution in transparent anhydrous plates, which closely resemble chlorate of potassa, but by ex-

posure to a moist air are gradually converted without any change of form into bicarbonate of potassa, while ammonia is evolved. It is readily dissolved by cold water, in which it spontaneously decomposes into bicarbonate of potassa and ammonia; a change which is accelerated by the application of heat. Fuses at a high temperature without loss of weight to a clear liquid, which, upon cooling, forms an opaque crystalline mass. If a concentrated solution be partially decomposed by acetic acid, or a dilute mineral acid, the acid cyanurate of potassa is precipitated.

Formula = KO, CyO ; eq. = 81.54.

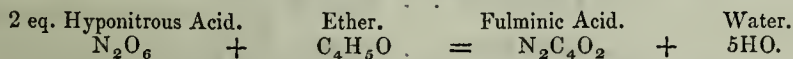
Cyanates of oxides of silver and lead are white anhydrous salts, which are insoluble in water, and are obtained by precipitating the cyanate of potassa by a neutral salt of lead or silver. Both consist of an eq. of acid and one of metallic oxide; the silver salt is soluble in ammonia, with which it forms a white crystalline compound, but by heat the ammonia is again evolved, and the pure cyanate of silver remains; decomposed by heat when dry, with a slight explosion, into cyanic acid, carbonic acid, nitrogen and dicyanide of silver.

The formulæ are AgO, CyO , and PbO, CyO .

FULMINIC ACID.

Hist.—Shown by Gay-Lussac and Liebig to be the constituent of the fulminating silver and mercury discovered by Howard.

Prep.—This acid is formed when nitrate of silver or protoxide of mercury, with an excess of nitric acid, is boiled in alcohol; aldehyd with nitric ether is evolved, and a white crystalline precipitate, the fulminate of silver or mercury, is deposited from the hot solution. By the action of the nitric acid upon the alcohol, hyponitrous acid on the one hand, and aldehyd and oxalic acid on the other, are produced. The presence of the oxide of silver or mercury effects a reaction between two eq. of hyponitrous acid and one of ether in the alcohol, by which they are converted into water and fulminic acid.



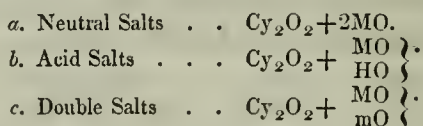
If a stream of hyponitrous acid vapour be conducted into a solution of nitrate of silver in alcohol, a copious precipitate of fulminate of silver is instantly formed.

Prop.—A bibasic acid; cannot be obtained in a free state from any of its salts, being decomposed at the moment of its separation by any other acid into hydrocyanic acid and a new product. The fulminate of silver is decomposed by hydrochloric acid into chloride of silver, hy-

drocyanic acid, and a new acid containing chlorine, the hydro-chloro-cyanic acid; similar effects are produced with hydriodic or hydrosulphuric acid. Oxalic and sulphuric acids decompose the salts of silver and copper without effervescence, hydrocyanic acid, ammonia, and other products not yet examined, being formed.

Formula is $Cy_2O_2, 2HO = C_4N_2O_2 + 2HO$; eq. = 68.78.

Fulminates.—The salts of fulminic acid contain either two atoms of a fixed base (neutral salts), or one atom of a fixed base and one atom of water (acid salts). The two atoms of fixed base must either be two atoms of the same or of two different metallic oxides, which are readily reduced, (2 eq. of CuO , 2 of HgO , 2 of AgO , or 1 eq. of CuO and 1 eq. of AgO , &c.) or 1 eq. of an easily reduced oxide with 1 eq. of an alkali (1 eq. AgO and 1 eq. KO or BaO , or ZnO , &c.) Fulminates with two atoms of a difficultly reduced metallic oxide cannot be obtained. From this it follows that when a salt of the first class,—such, therefore, as contain 2 eq. of oxides of silver, mercury, or copper,—are brought into contact with an alkali, only one half of the metallic oxide is replaced by its equivalent of the alkali; the other half remains in the new compound. This remarkable property seems to indicate a more intimate connexion between the acid and the oxygen of the metallic oxide which is combined with it, than is usually considered to exist. It has already been mentioned, that the salts may be considered as compounds of metals with certain radicals, which arise from the union of the oxygen of the base with the constituents of the anhydrous acid: when, therefore, it so happens that the affinity of the metal for the oxygen with which it is united predominates, it is impossible that the radical should be formed, or, what is the same thing, its decomposition must follow whenever an attempt is made to separate a metallic oxide, which is easily reduced, by one holding its oxygen by a powerful affinity. The composition of the fulminates may be expressed by the following general formulæ:—



Fulminate of Protoxide of Mercury.—Discovered by Howard.—Prepared by dissolving 1 part of mercury in 12 parts of nitric acid of sp. gr. 1.36, and adding to the solution 11 parts of alcohol of 80 — 85 per cent.; the mixture must be heated in a water-bath. The fluid soon enters into powerful chemical action; metallic mercury is precipitated, and nitric ether vapours evolved, the latter carrying off along

with them a considerable portion of the former; after a short time, hard opaque crystals of fulminate of mercury are deposited. These are carefully washed and dried at common temperatures on paper. It is freed from the admixture of metallic mercury by being redissolved in boiling water, from which it is deposited in white fine acicular crystals of a soft silky appearance. Explodes with great violence when struck or rubbed between two hard substances; placed on a red-hot coal, it burns with a slight explosion and a blue flame. It is used for firing the percussion guns: for this purpose, 10 parts of the salt are reduced to a fine powder by rubbing it with a wooden pestle on a marble slab with 30 parts of water; and this, when mixed with 6 parts of nitre, forms a paste, with which the copper caps are filled. The preparation of this salt is very dangerous, and the late distinguished chemist, Mr. Hennell, was killed by an explosion which occurred while he was preparing a large quantity with every precaution. The immediate cause of the explosion is unknown.

Formula = $2\text{HgO}, \text{Cy}_2\text{O}_2$; eq. = 488.78.

Fulminate of Silver.—*Prep.*—By dissolving 1 part of silver in 10 of nitric acid of sp. gr. 1.36—1.38 at a gentle heat, adding the mixture to 20 parts of alcohol of 85 to 90 per cent., and heating the mixture gently; as soon as the fluid begins to boil, it is removed from the fire, and placed aside to cool. The solution loses its transparency, and deposits the fulminate of silver in fine acicular crystals of a snow-white colour and of great lustre; when washed and dried, their weight should equal that of the silver used.

Prop.—The fulminate of silver is sparingly soluble in cold, but perfectly soluble in 36 parts of boiling water; is not decomposed by nitric acid; more readily exploded than the mercurial salt by friction, a blow, or by contact with concentrated sulphuric acid. Caustic alkalis separate half the silver as oxide; chloride of barium or potassium, as chloride; crystalline salts with two bases are obtained, from which the acid fulminate of silver may be separated by nitric acid; the latter salt may be obtained in crystals, and is more soluble than the neutral fulminate of silver.

Formula = $2\text{AgO} + \text{Cy}_2\text{O}_2$.

Fulminate of Copper.—Prepared by digesting the fulminates of silver or mercury with metallic copper. It may be obtained in green crystals, which are very soluble, and explode with a green flame.

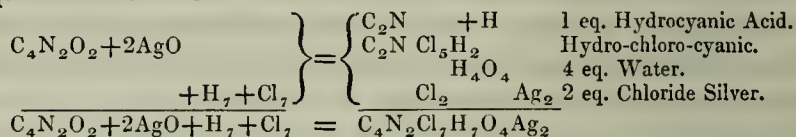
Formula = $2\text{CuO}, \text{Cy}_2\text{O}_2$.

Fulminate of Zinc.—According to E. Davy, by digesting the fulminate of mercury with metallic zinc. From the solution, which no longer contains a trace of mercury, baryta precipitates half the zinc,

and the fulminate of zinc and baryta $\left\{ \begin{smallmatrix} \text{ZnO} \\ \text{BaO} \end{smallmatrix} \right\} \text{Cy}_2\text{O}_2$ is obtained; from this the baryta may be precipitated by free sulphuric acid, and the acid fulminate of zinc remains in solution, which has been described by E. Davy as pure fulminic acid, but the presence of the zinc may be shewn, after the decomposition of the fulminic acid, by the sulphuret of ammonium and the known reagents (Fehling).

Hydro-chloro-cyanic acid.—Product of the decomposition of fulminate of silver by hydrochloric acid. If hydrochloric acid be added in successive portions to a mixture of fulminate of silver and water the acid fulminate is at first produced; but this salt is afterwards decomposed by the hydrochloric acid into chloride of silver, hydrocyanic acid, and a new acid composed of chlorine, cyanogen, and hydrogen. This substance has a styptic but sweetish taste, does not precipitate silver salts, and is decomposed by heat into carbonate of ammonia and other new products. The same change takes place when it is neutralized by potassa, and the solution evaporated. It contains 5 eq. of chlorine, and its constitution is most probably represented by the formula, $\text{C}_2\text{NCl}_5 + \text{H}_2$.

One eq. of fulminate of silver is decomposed with 7 eq. hydrochloric acid into water, 2 eq. chloride of silver, 1 eq. hydrocyanic acid, and 1 eq. of the new acid.



CYANURIC ACID.

Hist.—Described by Scheele as pyro-uric acid, by Serullas as cyanic acid, but its nature was first pointed out by Wöhler and Liebig.

Prep.—It is a product of the decomposition of the solid chloride of cyanogen by water, of the soluble cyanates by dilute acids (acetic, &c.), of urea by heat, of uric acid by the destructive distillation, and of melam, melamine, ammelide, and ammeline by acids. It is best prepared by dissolving dry melam in strong sulphuric acid, by aid of a gentle heat, throwing the solution into 20-30 parts of water; the mixture must be kept for several days at near its boiling heat, until upon trial it no longer gives a white precipitate with ammonia, when the solution may be evaporated to crystallize; the crystals should be purified by a second crystallization. Or it may be made by heating urea beyond its point of fusion, until it is converted with the evolu-

tion of ammonia into a white or greyish-white dry mass; this must then be dissolved in concentrated sulphuric acid, the solution treated with nitric acid added drop by drop until it becomes colourless, and then added to an equal volume of water; when cold, crystals of pure cyanuric acid are deposited.

By dissolving melam in strong sulphuric acid it is converted into ammelide, which, by being further heated, is converted into ammonia and cyanuric acid. $1 \text{ eq. melam} = \text{C}_{12}\text{N}_{11}\text{H}_9 + 6 \text{ eq. water} = 6\text{HO}$, yields 1 eq. ammelide , $\text{C}_{12}\text{N}_9\text{H}_9\text{O}_6 + 2 \text{ eq. ammonia}$, 2NH_3 ; and ammelide, in presence of diluted sulphuric acid, is resolved into $2 \text{ eq. cyanuric acid}$, $2(\text{C}_6\text{N}_3\text{O}_3)$ and 3 eq. ammonia , 3NH_3 . Three atoms of urea contain the elements of $1 \text{ eq. of cyanuric acid}$, and 3 eq. of ammonia ; at a high temperature the greater part of the ammonia is evolved as a gas, while a small portion remains in combination with the cyanuric acid.

Prop.—Colourless, inodorous, a slight taste, reddens litmus feebly, sparingly soluble in cold, but taken up by 24 parts of boiling water; the crystals from the aqueous solution contain 21.66 per cent. $= 4 \text{ eq. water}$, which they lose at common temperature when exposed to the air, but more rapidly when heated, and fall into powder. They are oblique rhombic prisms. The dry acid contains 3 eq. of water ; it may be obtained in crystals free from water of crystallization from a hot saturated solution in nitric or hydrochloric acid. The hydrate when heated is converted into $3 \text{ eq. of hydrated cyanic acid}$, the constituents of which it contains. It is soluble in the strongest acids without decomposition, but by long-continued boiling is converted into ammonia and carbonic acid.

It is a tribasic acid; its hydrate is $\text{Cy}_3\text{O}_3 + 3\text{HO}$; $\text{eq.} = 130.17$.

Cyanurates.—The salts of cyanuric acid contain three atoms of base, which are represented in the hydrate by three atoms of water; the oxides of the alkaline metals form salts which contain $1 \text{ or } 2 \text{ eq. of fixed base}$, with $2 \text{ or } 1 \text{ eq. of water}$, exactly as in the compounds of phosphoric acid; salts with $3 \text{ eq. of a difficultly reduced metallic oxide}$ cannot be procured; the silver salt alone contains $3 \text{ eq. of metallic oxide}$, and is anhydrous; in this state it has the same composition in the 100 parts as the cyanate and fulminate of silver. All cyanurates are decomposed by hydrochloric, nitric acids, &c.; the cyanuric acid crystallizes out of the solutions without retaining a trace of the metallic oxide with which it was united. Its alkaline salts fuse when heated, leaving a cyanate of the alkali, while cyanate of ammonia, cyanic and carbonic acids, are evolved. The general formulæ of the cyanurates are, therefore, as follow:—

- a. Salts with 1 eq. of fixed base $\text{Cy}_3\text{O}_3 + \frac{2\text{MO}}{2\text{HO}} \}$.
 b. Salts with 2 eq. of fixed base $\text{Cy}_3\text{O}_3 + \frac{\text{MO}}{\text{HO}} \}$.
 c. Salts with 3 eq. of fixed base or Neutral Salts $\text{Cy}_3\text{O}_3 + 3\text{MO}$.

Cyanurate of Ammonia.—White, brilliant prisms, which effloresce in the air, and lose ammonia when heated; dried in vacuo, they contain the constituents of 1 eq. of hydrated cyanuric acid, 1 of ammonia, and 1 of water.

Cyanurate of Potassa.—The salt $\left\{ \frac{2\text{HO}}{\text{KO}} \right\} + \text{Cy}_3\text{O}_3$ is made by neutralizing a boiling saturated solution of cyanuric acid by potassa; it falls in the form of white brilliant cubes. If these crystals be dissolved in a solution of caustic potassa, the addition of alcohol precipitates the cyanurate of potassa with two equivalents of fixed base, $\left\{ \frac{\text{HO}}{2\text{KO}} \right\} + \text{Cy}_3\text{O}_3$, in white acicular crystals. On being redissolved in water and evaporated, it is decomposed into free potassa and the former salt.

Cyanurate of Silver.—If nitrate of silver be added to either of the above salts of potassa, a white precipitate is obtained, which is cyanurate of silver, with 2 eq. oxide of silver and 1 eq. water, $\left\{ \frac{\text{HO}}{2\text{AgO}} \right\} \text{Cy}_3\text{O}_3$; this salt heated in the dry state evolves hydrated cyanic acid. But if a solution of silver be added to a boiling solution of cyanurate of ammonia, containing ammonia in excess, the cyanurate with 3 eq. of oxide of silver is formed, $3\text{AgO}, \text{Cy}_3\text{O}_3$; it is insoluble in water; very sparingly soluble in dilute nitric acid; may be heated to 600° without decomposition; is white, is not blackened by light, emits carbonic acid and nitrogen gases at a red heat, leaving the cyanide of silver as a residue.

CYAMELIDE, OR INSOLUBLE CYANURIC ACID.

The hydrate of cyanic acid, when free from water of crystallization, hardens shortly after its preparation into a white porcelain-like body, which is insoluble in water, dilute acids, alcohol, and ether; but is dissolved with decomposition by the caustic alkalis; ammonia is evolved, and cyanate and cyanurate of the alkali formed. Concentrated sulphuric acid dissolves it with the aid of heat, when with the elements of 2 eq. water it is decomposed into carbonic acid and ammonia; submitted to the destructive distillation, it is converted into

hydrated cyanic acid, a change which is very readily accounted for, since its composition is the same as that of the hydrated acid.

Probable formula is $C_2O_2 + NH = 43.39$.

CYANOGEN AND HYDROGEN.

HYDROCYANIC ACID, PRUSSIC ACID.

Hist.—Discovered by Scheele; for a knowledge of its nature and chemical properties we are indebted to Gay-Lussac; is a constituent of the water distilled from the leaves and blossoms of several stone-fruits; is formed by the destructive distillation of many substances containing nitrogen, by the decomposition of formate of ammonia by heat, and of the metallic cyanides by acids.

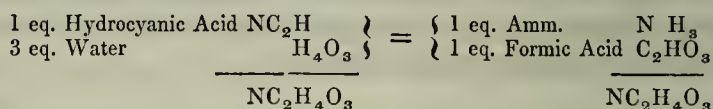
ANHYDROUS HYDROCYANIC ACID.

Prep.—Fifteen parts of crystalline ferricyanide of potassium are distilled in a retort, at a very gentle heat, with a mixture of 9 parts of sulphuric acid and 9 parts of water, and the products collected in a well-cooled receiver, containing 5 parts of chloride of calcium in coarse fragments: the mixture of acid and water should not be used till perfectly cold. The distillation is stopped as soon as the chloride of calcium is perfectly covered by the fluid collected in the receiver. It is then poured off into a strong glass vessel with a good stopper (Trautwein). It can also be prepared by decomposing the bichloride of mercury by strong hydrochloric or dry hydrosulphuric acid gas.

The ferrocyanide of potassium contains the cyanide of potassium, which is decomposed by the hydrous sulphuric acid into sulphate of potassa and hydrocyanic acid, according to the equation $KCy + HO, SO_3 = HCy + KO, SO_3$; the latter passes over with a little water into the receiver, but this is absorbed by the chloride of calcium.

Prop.—At common temperatures, a clear limpid fluid, very combustible, burning with a reddish flame, of sp. gr. = 0.6969 at 64°. It congeals at 5° to a solid fibrous mass, boils at 80°, may be mixed in every proportion with water, ether, and alcohol; the sp. gr. of the vapour is 0.9476: scarcely reddens litmus paper. It has a peculiar penetrating odour, said to be similar to that of bitter almonds, but this is because oil of bitter almonds contains it, the smell being very different in reality; checks the breathing, and causes a flow of tears: it possesses a penetrating taste, which is somewhat burning, and strongly bitter; its vapour, when inhaled, acts instantly as a most powerful

poison. The antidotes are ammonia, as likewise chlorine, which, however, must be administered with caution. The congelation of the acid at 5° is, according to Schulz, owing to small quantities of water; he states the perfectly anhydrous acid as still liquid at -64° . Decomposes when perfectly pure with the greatest facility under the influence of light, with the formation of a brown substance and ammonia; small quantities of acids prevent this decomposition; by concentrated mineral acids it is very rapidly converted, together with the elements of water, into formic acid and ammonia; 3 eq. of water and 1 of hydrocyanic acid, a strong acid being present, suffer mutual decomposition and are converted into ammonia which unites with the acid, and into formic acid.



Potassium heated in the vapour of the acid unites with the cyanogen, and liberates the hydrogen; lime and baryta, when heated in the vapour, also liberate hydrogen and give rise to cyanates; it is decomposed by chlorine with the formation of hydrochloric acid and chloride of cyanogen.

HYDROUS HYDROCYANIC ACID.

Prep.—One part of bicyanide of mercury dissolved in 8 parts of water is treated with a stream of sulphuretted hydrogen gas till the latter is in slight excess; the free sulphuretted hydrogen removed by a little carbonate of lead, and filtered. The clear liquid contains $\frac{1}{40}$ of anhydrous hydrocyanic acid. By the decomposition of the bicyanide of mercury the fluid becomes black like ink, and it frequently only becomes clear after the addition of a small quantity of a free mineral acid; it contains too, very generally, small quantities of hydrosulphocyanic acid. It may be prepared of the same strength and perfectly pure, according to Geiger, by distilling 4 parts of crystallized ferrocyanide of potassium with 18 parts of water and 2 of strong sulphuric acid; 20 parts of water are placed in the receiver, and the distillation is conducted until 38 parts have collected. The distillation is best conducted in a chloride of calcium bath, and the vapours should be condensed by a condensing apparatus of glass. The product is collected in a cylindrical bottle, which is marked at the point corresponding to 38 parts.

According to Clark, it may be prepared by dissolving 1 part of tartaric acid in 40 parts of water, and adding $2\frac{2}{3}$ parts of pure cyanide of potassium in coarse fragments to the solution. The fluid must be

kept very cold, and shaken from time to time; this acid contains 3 per cent. anhydrous acid, and $2\frac{1}{2}$ to 3 grs. of bitartrate of potassa in the ounce.

Magendie states that the medicinal hydrocyanic acid is prepared by mixing 1 part by volume of the anhydrous acid with 6 parts of water; or, by weight, 1 part of the acid with $8\frac{1}{2}$ of water. But this would yield an acid containing 12 per cent. of the anhydrous acid, which is four times stronger than the acid usually employed in Britain.

All methods in which hydrocyanic acid is obtained by distillation never yield this energetic preparation of the same quality and strength; even with the application of every possible precaution, the product never contains more than four-fifths of the small quantity of acid which, according to the calculation, ought to be procured; this arises, when ferrocyanide of potassium is used, from a portion of the cyanide entering into combination with the protocyanide of iron during the decomposition of the yellow salt, or from the impossibility of effecting an absolute condensation of so volatile a substance during the distillation. It is therefore greatly preferable to prepare a stronger acid in the first instance, to determine by experiment the quantity of anhydrous acid contained in it; and by the addition of water to bring it to that degree of dilution which is prescribed by the physician, or by the medical laws of the land. For example, 2 parts of crystalline ferrocyanide of potassium are distilled with 1 part of sulphuric acid and 2 of water to dryness in a chloride of calcium bath; and the product, well cooled by the condensing tube apparatus, collected in a narrow-mouthed bottle, into which 2 parts of water have been placed. The quantity obtained generally amounts to $4-4\frac{1}{2}$ parts by weight of liquid, containing, according to the more or less perfect cooling, from 17—20 per cent. of anhydrous hydrocyanic acid. The exact quantity is determined in the following manner:—One drachm = 60 grs. of the dilute acid is added to a carefully balanced glass vessel, which contains a dilute solution of nitrate of silver, and the increase of weight accurately determined; by way of precaution, a trial is made to see whether the addition of the silver solution causes a further precipitation, the precipitate collected upon a weighed filter, washed, dried, and the quantity of cyanide of silver determined by a second weighing. Five parts of the precipitate correspond to 1 part of the hydrocyanic acid. If, for example, 52 grains of cyanide of silver be obtained, the 60 grains of dilute acid would have consisted of 10.4 grains of anhydrous acid, and of 49.6 grains of water. Where it is desired, according to the prescription of any pharmacopœia, to make a hydrocyanic acid containing 3 per cent. of anhydrous acid, and consequently 97 per

cent. of water, it is done in the following manner:—3 hydrocyanic acid is to 97 water as 10·4 acid is to $X = 336\cdot2$ water; to 10·4 grains of anhydrous acid 336·2 grains of water must be added, in order to form a mixture which shall contain 3 per cent. of anhydrous acid. To each drachm of the product, therefore, since it consists of 10·4 grains of anhydrous acid and 49·6 of water, $336\cdot2 - 49\cdot6 = 286\cdot6$ grains of water must be added. This method may be used for testing the strength of any solution of hydrocyanic acid; 100 grains of an acid which contains 3 per cent. anhydrous prussic acid should, when precipitated by the nitrate of silver, give 15 grains of the cyanide. This method is independent of all accidents which can possibly have an influence upon the activity of the preparation; it is so very simple that it will yield accurate results in every hand. The peroxide of mercury which is readily dissolved at common temperatures, may also be used to test the strength of the aqueous acid; a drop or two of caustic potassa is added to the solution, which is then treated with a known weight of the peroxide in fine powder; every 4 parts of the oxide dissolved corresponds to one of the anhydrous acid. Testing with green vitriol must be entirely rejected.

Prop.—The properties of the aqueous acid are similar to those of the concentrated, with the difference of taste, odour, and poisonous and combustible properties, which are dependent on a higher or lower degree of concentration; it decomposes when perfectly pure as readily as the anhydrous acid, becoming brown, and at last black. Like the anhydrous acid, however, it may be preserved by adding a trace of a strong mineral acid; a slight permanent reddening of litmus paper should not therefore be considered a sufficient reason for rejecting an acid; it should be clear and colourless, leave no residue on evaporation, nor be precipitated or blackened by sulphuretted hydrogen. Treated with ammonia, and evaporated in a water-bath, the dry residue should not exceed one quarter per cent.; nor should it become brown when heated, this indicating the presence of formic acid, which may also be detected by the tests hereafter to be mentioned. Sulphuric acid is detected by baryta; hydrochloric acid by evaporating in a water-bath till all odour of prussic acid is gone, and then adding a salt of silver. By careful rectification over chalk, an excess of mineral acids may readily be corrected; but in this case a trace of hydrochloric or sulphuric acid must be added afterwards, to give stability to the acid.

Its formula is CyH ; eq. = 27·39.

Hydrocyanate of Ammonia, Cyanide of Ammonium.—Prepared by distilling dry ammoniacal salts with metallic cyanides, or by bringing

anhydrous hydrocyanic acid into contact with ammoniacal gas, when the compound is produced in the form of bright crystalline plates. It is almost as volatile as the acid itself; decomposes very rapidly in water, is poisonous, and has a strong peculiar smell.

Formula is NH_4Cy ; eq. = 44.54.

HYDROCYANIC ACID WITH METALLIC OXIDES.

On bringing hydrocyanic acid into contact with metallic oxides which retain their oxygen by a feeble affinity, as in the oxides of mercury, silver, and palladium, they suffer mutual decomposition, giving rise to the formation of water and a metallic cyanide; if no water be present, the decomposition is accompanied by so great an evolution of heat as to cause an explosion. The alkaline oxides unite with the acid without decomposition, they retain their alkaline re-action, and the solution has the odour of the acid; but also in this class of compounds the decomposition of the acid and alkali is instantly effected, when the solution is treated with another metallic cyanide, with which they form a double compound. With many oxides, as, for example, with the oxide of copper, the hydrocyanic acid gives rise to a corresponding cyanide; but this is decomposed either instantly, or after a short time, into cyanogen gas, and a subcyanide; with the peroxide of lead the protocyanide is formed, and cyanogen liberated.

The compounds of cyanogen with silver, mercury, and most heavy metals, are not decomposed by dilute ox-acids, and are with difficulty decomposed by concentrated nitric acid at a boiling temperature; many of them with great facility by hydrosulphuric and hydrochloric acid into hydrocyanic acid, and a metallic sulphuret or chloride (cyanides of mercury, silver). The cyanides of the precious metals (silver, mercury) are decomposed by heat like the corresponding oxides into cyanogen and metal; the cyanides of the heavy metals into a carburet and free nitrogen; the cyanides of the alkaline metals, if protected from the action of the air and moisture, will bear a very high temperature without decomposition. All insoluble cyanides of the heavy metals may be formed by adding hydrocyanic acid to the acetate. They are decomposed on being heated in a large excess of hydrochloric acid or in hydrate of potassa into a metallic chloride, or into an oxide, ammonia, and formic acid; the latter is the case with the alkaline cyanides when boiled in an excess of alkali. All metallic cyanides, the corresponding oxides of which do not retain carbonic acid at a red heat, evolve, when burnt with oxide of copper, nitrogen and carbonic acid gases in the proportion 1 : 2 by volume.

Cyanide of Potassium.—Formed, when potassium is heated in cyanogen gas with the appearance of combustion, by heating potassium with anhydrous substances containing nitrogen, by heating the carbonate of potassa to redness with matter containing carbon and nitrogen.

Prep.—By adding hydrocyanic acid in excess to a recently prepared concentrated solution of caustic potassa, evaporating the solution in a retort at a boiling heat till crystallization commences, when it must be poured into a porcelain dish and fused at a low red heat. Or a saturated alcoholic solution of hydrate of potassa is treated with the vapour of hydrocyanic acid as long as it throws down a white crystalline precipitate, which should be washed with alcohol and dried. An additional quantity is obtained by evaporating the liquid in a retort; or, better, by heating the ferrocyanide of potassium, carefully dried and reduced to a fine powder, in an iron vessel or well-closed crucible to a strong red heat, exposure to the air being carefully avoided till quite cold; the semi-fused or black porous mass must then be reduced to a fine powder, placed in a funnel, moistened with a little alcohol, and then washed with cold water. The first concentrated colourless solution which passes off, is rapidly brought to dryness and fused in a porcelain dish. The pounded fused mass may also be boiled in spirit when the cyanuret is deposited in crystals on cooling. Alcohol of 60 per cent. dissolves at the boiling temperature a considerable quantity of the cyanide, almost the whole of which is again deposited as the solution cools; if it be stronger or weaker, this does not occur. The application of warm water in the preparation must be altogether avoided, as when air is present it at once colours the solution yellow, owing to the reproduction of the ferrocyanide of potassium.

Prop.—Colourless; crystallizes in transparent cubes, or other forms of the octohedral system, without odour, but of a sharp biting alkaline and bitter-almond taste; fuses readily to a clear transparent liquid, and will bear a white heat without decomposition in close vessels; exposed to oxygen, on the contrary, it is converted into cyanate of potassa. On exposure the crystals become opaque, deliquesce in a moist atmosphere, are very soluble in water, the solution is decomposed even by the carbonic acid of the air, and smells of prussic acid. Even kept in close vessels it decomposes in a shorter or longer time.

The cyanide of potassium is converted, when dissolved in water, into hydrocyanate of potassa; if the solution be evaporated with an excess of potassa, the whole of the nitrogen is evolved as ammonia, and formate of potassa remains. Effervescence on the addition of an acid proves the presence of carbonic acid; a yellow colour, that of iron; and a blackening when heated, the admixture of salts of

formic acid. It may be used in medicine instead of the hydrocyanic acid.

Formula = KCy ; eq. = 65.54.

Liebig gives the following process, by which there is obtained with the utmost facility a cyanide of potassium which, although not quite pure, contains only a little cyanate of potash, an impurity which does not interfere with its use as a most energetic reducing agent, whether used as a flux in the dry way, or in solution ; 8 parts of dried ferrocyanide of potassium, and 3 of pure carbonate of potash, are fused together in an iron or earthen crucible, till the iron is entirely separated as a grey spongy mass, and the fused salt appears quite colourless on cooling. It is then poured off from the iron, and when solid broken up and carefully preserved in well closed vessels.

In this process, if we suppose 1 eq. of the ferrocyanide, and 1 eq. of the carbonate to be fused together, $(\text{FeCy} + 2\text{KCy})$, and $(\text{KO} + \text{CO}_2)$, the 2 eq. of cyanide of potassium in the ferrocyanide remain unchanged, while the cyanide of iron, FeCy is acted on by the carbonate. Now the re-action between cyanide of iron and carbonate of potash is as follows :— $2\text{FeCy} + 2\text{KO},\text{CO}_2 = \text{Fe}_2 + \text{KO},\text{CyO} + \text{KCy} + 2\text{CO}_2$; that is, the iron is reduced, and half the potassium of the carbonate is obtained as cyanide of potassium, the other half as cyanate of potash, while the carbonic acid is expelled. Hence the presence of cyanate of potash ; and it is plain that with 1 eq. ferrocyanide, and 1 eq. carbonate, we shall obtain $2\frac{1}{2}$ eqs. of cyanide of potassium, and $\frac{1}{2}$ eq. of cyanate of potash ; or doubling the quantities, because as we have just shown, the re-action between the cyanide of iron and the carbonate of potash requires 2 eq. of each, the result is 5 eq. cyanide of potassium to 1 eq. cyanate of potash. Thus, $2(\text{FeCy}, 2\text{KCy}) + 2(\text{KO}, \text{CO}_2) = \text{Fe}_2 + 5\text{KCy} + \text{KO}, \text{CyO} + 2\text{CO}_2$. Since the eq. of cyanide of potassium is about 66, and that of cyanate of potash about 82, it is evident that the proportion of the latter salt to the former, in Liebig's cyanide, must be 82 to 330, or almost exactly 1 to 4.

Liebig's cyanide of potassium, thus prepared, is a salt of the highest value to the chemist. It possesses, in the dry way, and at comparatively low temperatures, a most remarkable reducing energy, deoxidising by virtue of its potassium as well as by virtue of the carbon contained in its cyanogen. Many metals, such as iron, lead, arsenic, antimony, and others much less easily reducible, are instantly reduced by this salt at a red heat ; and from its great fusibility it acts as a flux, admitting of the ready collecting of the reduced metal into a button.

In solution it is a most valuable means of detecting and separating from each other a number of metals, and is now much used. For de-

tails as to its use the reader is referred to the papers of Liebig, and of Fresenius and Haidlen, in the "Annaler den Chemie et Pharmacie."

Cyanide of sodium may be prepared in the same manner, and has the same properties as the cyanuret of potassium. Formula = NaCy .

Cyanide of Zinc.—*Prep.*—Metallic zinc is dissolved by the aid of heat in acetic acid, and the acid solution treated with hydrocyanic acid as long as a precipitate is formed; the latter must then be washed and dried.

Prop.—A brilliant white, tasteless powder, insoluble in water and alcohol, but perfectly soluble in ammonia, as also in dilute hydrochloric acid with the evolution of hydrocyanic acid.

Formula = ZnCy ; eq. = 58.69.

Cyanide of Iron.—This compound, remarkable from its tendency to form a very peculiar class of double compounds by uniting with other cyanides, would appear as incapable of existing in a free state as the corresponding protoxide. On adding a proto-salt of iron to a solution of cyanide of potassium, a yellowish-red precipitate is formed, which is re-dissolved by an excess of the cyanide into a yellow liquid, the ferrocyanide of potassium. On heating dry ferrocyanide of ammonium, cyanide of ammonium is evolved, and a grey insoluble powder, which has been considered as this compound, is the residue obtained. It is also produced, according to Robiquet, by pouring a saturated solution of hydrosulphuric acid over recently precipitated Prussian blue contained in a well-stoppered vessel; the Prussian blue becomes white, and the solution contains hydrocyanic acid. (Berzelius.) The properties of these preparations differ too widely to allow of their being considered as identical. Formula = FeCy ; eq. = 54.39.

Sesquicyanide of Iron.—Unknown in a pure state. On adding a solution of ferridecyanide of potassium to the silico-fluoride of iron, the silico-fluoride of potassium is separated, and a deep brown liquid remains, which has a strong astringent taste, becomes blue on evaporation, and leaves a residue of Prussian blue. It forms a numerous class of double cyanides. Its formula is Fe_2Cy_3 ; eq. = 135.17.

$\frac{4}{3}$ *Cyanide of Iron.*—This compound is obtained by boiling the green powder, which falls on heating or exposing to the air a solution of ferrocyanuret of potassium charged with an excess of chlorine gas, with 8 — 10 times its weight of concentrated hydrochloric acid, until the filtered solution ceases to be rendered turbid by water. The green residuc, when well washed, should be dried in vacuo; it is but slightly acted upon by concentrated hydrochloric acid, or by chlorine, but it is readily decomposed by hydrate of potassa into peroxide of iron and ferrocyanide and ferridecyanide of potassium. (Pelouze.)

Its formula is $\text{FeCy} + \text{Fe}_2\text{Cy}_3 + 4 \text{ aq.}$

Cyanide of Cobalt.—Formed by mixing a solution of the acetate of cobalt with hydrocyanic acid. It is a brownish-white precipitate.

Formula = CoCy ; eq. = 55.89.

Bicyanide of Mercury.—*Prep.*—An aqueous solution of prussic acid is treated with finely powdered peroxide of mercury until all odour of the former disappears ; the liquid yields on evaporation perfectly pure crystals of the bicyanide. For this purpose the acid prepared as recommended by Geiger is most convenient ; it should be introduced into a well-stoppered bottle, and the combination with the oxide of mercury promoted by frequent agitation. It must always be remembered, that the compound can only be produced when water is present in sufficient quantity to dissolve the whole of the cyanide ; water must therefore be added, should it be observed that the liquid smells of prussic acid, while any portion of the oxide of mercury remains undissolved. Or by adding to a solution of 2 parts of ferrocyanide of potassium in 15 parts of boiling water, 3 parts of perfectly dry bisulphate of the peroxide of mercury ; boil the mixture for a quarter of an hour, and separate the clear liquid while boiling hot from the precipitate by filtration ; as the solution cools, the bicyanide crystallizes. The mother-liquor yields a second crop of crystals by further concentration ; or it may be evaporated to dryness, and the cyanide obtained from the residue by boiling alcohol. The first crystals from the aqueous solution are purified by a second crystallization. The formation of the cyanide in this process is owing to the mutual decomposition between the 2 eq. of cyanide of potassium of the ferrocyanide and 2 eq. of persulphate of mercury into bicyanide of mercury and sulphate of potassa, while the cyanide of iron is precipitated.

Prop.—Crystallizes in colourless regular four or six-sided prisms, sometimes transparent, but oftener opaque ; they are anhydrous, permanent in the air, of a very disagreeable metallic taste, and are very poisonous. Is dissolved by 8 parts of water at 60° , but is more soluble in boiling water, and in alcohol.

Peroxide of mercury decomposes all soluble metallic cyanides with the formation of an oxide and double cyanides of mercury and other metals. If the bicyanide be boiled with an excess of peroxide of mercury, the latter is dissolved in large quantity (3 eq. Kühn), and the solution on evaporation deposits a compound in fine acicular crystals ; these are more soluble in cold water than the bicyanide, and have an alkaline reaction on vegetable colours. The formation of this compound, during the preparation of the bicyanide, must be carefully avoided, or only a white saline mass may be obtained. This is best

done by the careful addition of hydrocyanic acid until its odour is slightly perceptible.

A cyanide corresponding to the protoxide of mercury is unknown. When an attempt is made to obtain it by adding a proto-salt of mercury to hydrocyanic acid, metallic mercury is instantly separated, and the bicyanide formed.

Formula is HgCy_2 ; eq. = 254.78.

Cyanide of Silver.—Falls, on mixing a soluble salt of silver with hydrocyanic acid, in the form of a brilliant white curdy precipitate; is decomposed by all hydracids, but with great difficulty by other mineral acids; strong boiling nitric acid alone can dissolve it; suffers no change by the caustic fixed alkalies, is readily dissolved by ammonia. It is soluble in a concentrated solution of the nitrate of silver, forming with it a compound, which may be obtained in crystals, but is not permanent in water. It gives rise to double compounds with all cyanides of the alkaline metals.

Formula is AgCy ; eq. = 134.39.

Cyanide of Palladium.—The affinity of palladium for cyanogen surpasses that of all other metals; they combine, whenever hydrocyanic acid or any soluble cyanide is added to a salt of the oxide of palladium, in the form of a light chesnut precipitate, which has a greenish tint if copper be present; gives rise to double salts with ammonia, cyanide of potassium, and nitrate of the oxide of palladium.

Formula PdCy ; eq. = 79.69.

Percyanide of Gold.—For the preparation of this compound, which has recently been used medicinally, a solution of gold in aqua regia, carefully deprived of all free acid by evaporation, is precipitated by a recently prepared solution of caustic potassa to which hydrocyanic acid has been added in excess; care must be taken that a small quantity of the chloride of gold remain in the solution. The yellowish-white precipitate is collected, washed, and dried. An excess of cyanide of potassium dissolves the precipitate, and the solution has a yellowish-red colour, but in this case it is re-precipitated by the addition of an acid. It may also be prepared by adding to 16 parts of gold dissolved in aqua regia by the aid of heat a boiling solution of 24 parts of bicyanide of mercury, evaporating to dryness, and washing with pure water. The cyanide corresponding to the oxide does not exist.

Its formula is AuCy_3 ; eq. = 278.17.

Cyanide of Platinum.—This compound is not known in a separate state, but appears to form some interesting double cyanides. See below.

DOUBLE CYANIDES OF THE METALS.

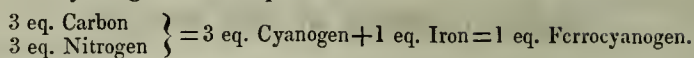
All insoluble metallic cyanides (of heavy metals) combine with the soluble (of alkaline metals) to peculiar generally crystallizable double compounds, which are very similar in their general properties to the combinations of the soluble and insoluble metallic sulphurets. For example, the cyanides of gold, palladium, silver, nickel, zinc, copper, &c., are readily dissolved by the cyanide of potassium or sodium; the solutions are either yellow or colourless, and are not changed or decomposed by the caustic or carbonated alkalies, or by metallic chlorides; acids cause the precipitation of the insoluble cyanide, owing to the decomposition of the soluble cyanide. On mixing a double cyanide of potassium or sodium with a metallic salt, the basis of which is an oxide of a heavy metal, a new double compound is generally formed, arising from the replacement of the alkaline metal by its equivalent of the heavy metal. The double cyanuret of silver and potassium, $\text{KCy} + \text{AgCy}$, forms, with acetate of lead, $\text{PbO}, \bar{\text{A}}$, the double cyanide of silver and lead, $\text{PbCy} + \text{AgCy}$, and acetate of potassa.

The soluble metallic cyanides also very frequently form double compounds with the insoluble metallic chlorides, bromides, and iodides.

The double compounds of both the cyanides of iron, of the cyanide of cobalt, and of the cyanides of some other metals, with other cyanides, and with hydrocyanic acid, are very remarkable in their properties: the latter are soluble in water, are crystallizable, are possessed of a distinct acid taste, produce a permanent reddening of the vegetable colours, decompose carbonates with effervescence, and perfectly neutralize the alkalies; properties not possessed by the free hydrocyanic acid. Neither the iron, the cobalt, nor the other analogous metals in these compounds can be detected by the alkalies, by the soluble metallic sulphurets, or, in short, by any of the ordinary reagents.

Constitution of the double compounds of Iron and Cyanogen.—The composition of these compounds is best explained by supposing the existence of a radical, which contains 1 eq. of iron in combination with carbon and nitrogen in the same proportion as they exist in cyanogen, but in such quantity as would form 3 eq. of the latter, and which radical, by uniting with 2 eq. of hydrogen, forms a bibasic acid. The radical itself may be called ferrocyanogen; the acid, hydroferrocyanic acid; and the compounds of the radical with the metals by the same adjuncts to ferrocyanide as are used for the corresponding oxides.

The ferrocyanogen is composed of



Its symbol is Cfy, and its compounds are

Hydro-ferrocyanic Acid	Cfy + H ₂
Ferrocyanide of Potassium	Cfy + K ₂
Ferrocyanides with two Basic Metals	Cfy + $\left\{ \begin{array}{c} K \\ Ca \end{array} \right\}$ or $\left\{ \begin{array}{c} K \\ Ba \end{array} \right\} \left\{ \begin{array}{c} K \\ Sr \end{array} \right\} \left\{ \begin{array}{c} K \\ Mn \end{array} \right\}$
Ferrocyanide of Potassium and Iron	2Cfy + $\left\{ \begin{array}{c} Fe_3 \\ K \end{array} \right\}$
Prussian Blue	2Cfy + 2Fe ₂
Basic Prussian Blue	3Cfy + $\left\{ \begin{array}{c} 2Fe_2 \\ Fe_2O_3 \end{array} \right\}$
Soluble Prussian Blue	2Cfy + $\left\{ \begin{array}{c} Fe_2 \\ K \end{array} \right\}$
Ferrocyanide of Zinc and Potassium	2Cfy + $\left\{ \begin{array}{c} Zn_3 \\ K \end{array} \right\}$

HYDRO-FERROCYANIC ACID.

Discovered by Porrett. Best prepared by mixing a cold saturated solution of ferrocyanide of potassium with as much strong hydrochloric acid as is sufficient to decompose it, and agitating the mixture with ether, which rises to the surface with the hydroferrocyanic acid as a white crystalline mass, which is to be dried with precaution to avoid the access of air. When dry it may be dissolved in alcohol, and the solution spontaneously evaporated.

Prop.—A white distinctly crystalline mass, or small granular, sometimes acicular crystals, which acquire a blue colour by exposure to the air. The aqueous solution is decomposed by boiling into hydrocyanic acid, and a white, but after exposure in open vessels blue, precipitate. The hypothetical radical of the acid can (probably) not be isolated. Its formula is Cfy + H₂; eq. = 109.17. This acid may be viewed as a compound of cyanide of iron with hydrocyanic acid, FeCy + 2HCy.

Ferrocyanide of Ammonium.—It may be formed by digesting at a gentle heat the ferrocyanide of lead with carbonate of ammonia; filtering to separate the carbonate of lead, and evaporating to crystallization. It is isomorphous with the ferrocyanide of potassium; the crystals are white, or yellowish-white, transparent, permanent in the air, very soluble in cold, but decomposed by boiling water into cyanide of ammonium and cyanide of iron, insoluble in alcohol. It forms with sal-ammoniac a double salt, which is obtained by boiling a solution of equal parts of ferrocyanide of potassium and sal-ammoniac in 6 parts of water, when it forms, on cooling, large lemon-yellow crystals, which are very brittle and permanent in the air. They are composed of an eq. of ferrocyanide of ammonium, 1 of sal-ammoniac, and 3 eq. of water. (Bunsen.)

HYDRO-FERROCYANIC ACID AND METALLIC OXIDES.

On bringing the hydro-ferrocyanic acid into contact with metallic oxides, the latter are reduced by the hydrogen of the acid, water, and a compound of the metal with the radical of the acid, being formed ; as 1 eq. of the acid contains 2 eq. of hydrogen, it follows as a necessary consequence that it decomposes 2 eq. of the most numerous class of oxides, in which 1 eq. of oxygen is present in 1 eq. of the oxide.

The ferrocyanides are, without exception, decomposed when exposed to a red heat in close vessels ; those which contain an alkaline metal give rise to the formation of the cyanide of that metal, a carburet of iron, and the evolution of nitrogen gas ; all others yield mixtures of metals and metallic carburets, with or without the evolution of cyanogen. All the soluble ferrocyanides are decomposed by being boiled with peroxide of mercury into bicianide of mercury, free alkali, and oxy-cyanide of iron. The ferrocyanides of potassium and sodium are converted by being calcined in open vessels into alkaline cyanates, and the black oxide or carburet of iron.

Most of the ferrocyanides contain water of crystallization, which they lose when heated. Those of zinc, copper, and mercury unite with ammonia to peculiar crystalline double compounds. (Bunsen.) Most of them are soluble in concentrated sulphuric acid without decomposition ; or they unite with it, when they lose their colour, to saline combinations, in which the ferrocyanide acts the part of a base. By nitric acid they are decomposed, many of them with the evolution of cyanogen and the formation of metallic ferrid-cyanides. When those which are soluble in water are boiled with dilute acids, the hydro-ferrocyanic acid is separated, and at that temperature decomposed into hydrocyanic acid, which escapes, and into the white but impure proto-cyanide of iron, which, on exposure to the air, absorbs oxygen and becomes blue.

Ferrocyanide of Potassium.—*Prep.*—This compound occurs of great purity in commerce, and is prepared on a large scale by fusing substances which are rich in nitrogen, as horn, hoof, and dried blood, with 2—3 parts of carbonate of potassa in iron vessels ; the mass after perfect fusion is allowed to cool, the soluble parts removed by boiling water, from which the ferrocyanide is obtained by crystallization. It may be obtained on a small scale by boiling Prussian blue in carbonate of potassa.

By the fusion of substances containing carbon and nitrogen with im-

pure carbonate of potassa or pearlash, at a red heat, the potassa is reduced by a portion of the carbon to potassium, by the reaction of which on the rest of the materials cyanide of potassium as the principal product is formed. The red-hot fused mass does not contain a particle of the ferrocyanide, but it contains, in the form of a black slime, a large quantity of finely divided metallic and carburetted iron, as well as sulphuret of iron, formed by the action of sulphuret of potassium, which is derived from the sulphate contained in the pearlash, on the oxide of iron of the blood, when dried blood is used, or that formed from the vessel. If the mass be treated with cold water, and the filtered solution evaporated, no ferrocyanide is obtained; but if, while covered with water, it is freely exposed to the air and gently warmed for some hours, iron is dissolved, and a yellow solution is obtained, which is rich in ferrocyanide of potassium; this arises from the solution of pure cyanide of potassium readily dissolving iron, or its sulphuret. In close vessels the solution of iron by cyanide of potassium is attended with the evolution of hydrogen, owing to the decomposition of water, the oxygen of which unites with the potassium, while the cyanogen passes over to the iron. The fused mass contains a large quantity of free potassa, which, by being boiled with the cyanide of potassium, causes the decomposition of the latter into formiate of potassa and ammonia; if the animal substances be fused in open vessels with the potassa, a portion of the cyanide of potassium is burnt into cyanate of potassa, the solution of which is decomposed by boiling into ammonia and bicarbonate of potassa. The ammonia arises in every case from the decomposition of the cyanide of potassium; its formation is consequently always accompanied by a corresponding loss, and should be most carefully avoided. For this reason, the air should be excluded as far as possible in the first stage of the process.

It is to the researches of Liebig that we are indebted for the true theory of this process; and the study of the conditions under which the salt is formed has thus led to very great improvements in its manufacture and to a great saving, more ferrocyanide being obtained from the same quantity of materials.

The action of cyanide of potassium on iron or its sulphuret may be thus expressed, $3\text{KCy} + \text{Fe} + \text{HO} = (2\text{KCy} + \text{FeCy}) + \text{KO} + \text{H}$; or $3\text{KCy} + \text{FeS} = (2\text{KCy} + \text{FeCy}) + \text{KS}$.

Perhaps the best method is to fuse the animal matter with pure carbonate of potash in close iron vessels, when, from the absence of sulphate (always present in pearlash) the vessels would not be attacked and corroded as they now are. The cyanide of potassium, dissolved in cold water, should now be digested with iron filings in open vessels,

when, by the reaction above explained, the whole of the cyanogen would be obtained as ferrocyanide.

Prop.—Crystallizes in large quadrangular tables or short prisms with truncated edges and angles, which belong to the square prismatic system; it is of a lemon-yellow colour, of sp. gr. 1.832; has at first a sweetish bitter, but afterwards a saline taste; is permanent in the air, loses at 212° 12.82 per cent. = 3 eq. of water, and becomes white; is soluble in 4 parts of cold and in 2 parts of boiling water; is insoluble in alcohol, by which it is precipitated from its aqueous solution in brilliant yellow flakes. Is converted by nitric acid, with the escape of cyanogen, and by chlorine, into the ferrid-cyanide of potassium. At a red heat it is decomposed into the carburet of iron and cyanide of potassium, but by the action of atmospheric air the latter is converted into cyanate of potassa.

The ferrocyanide of potassium forms double compounds with other ferrocyanides. It is used as a test for the oxide of iron in solution. When thus employed, however, it must be remembered that the solution must not have an alkaline reaction, for all solutions of oxide of iron which contain free alkali are not precipitated by the ferrocyanide of iron.

It is used for the preparation of hydrocyanic acid, bicyanide of mercury, Prussian blue, &c.; taken in large doses is purgative, and not poisonous.

The crystals are $K_2Cfy + 3 aq.$; eq. = 185.47.

It may also be viewed as a double cyanide of iron and potassium, $FeCy + 2KCy$.

Ferrocyanide of Sodium.—Prepared by boiling Prussian blue with carbonate of soda. Crystallizes in yellow quadrangular prisms, effloresces in the air, contains 59 per cent. = 12 eq. of water of crystallization, is soluble in $4\frac{1}{2}$ parts of cold water, is insoluble in alcohol.

Ferrocyanide of Barium.—Prepared by digesting Prussian blue in a solution of baryta. Is deposited from the boiling hot solution of small rhomboidal crystals of a yellow colour, is soluble in 100 parts of boiling and 1920 parts of cold water; loses at 100° 16.58, at higher temperatures 18 per cent. = 6 eq. of water; is soluble in concentrated sulphuric acid.

Ferrocyanide of Iron.—Unknown in pure state, but exists in the double ferrocyanides; see those of potassium.

Ferrocyanide of Lead.—Prepared by mixing a soluble salt of lead with ferrocyanide of potassium. Falls as a white precipitate with a shade of yellow. When dry it is anhydrous, Pb_2Cfy .

Ferrocyanide of Zinc.—Prepared by mixing a soluble salt of zinc

in solution with hydro-ferro-cyanic acid. It falls as a white precipitate.

Ferrocyanide of Copper.—Prepared by mixing a soluble salt of copper with ferrocyanide of potassium. A beautiful red brown precipitate, which is insoluble in dilute acids; a solution containing $\frac{1}{60000}$ of its weight of oxide of copper is readily recognized by the distinct reddish-brown colour produced by ferrocyanide of potassium.

Ferrocyanide of Mercury.—On mixing a solution either of protoxide or peroxide of mercury with ferrocyanide of potassium a white precipitate falls, which spontaneously decomposes into cyanide of mercury which is re-dissolved, and into cyanide of iron. This change is rendered more rapid by the aid of heat, and metallic mercury is separated when a proto-salt of mercury has been used.

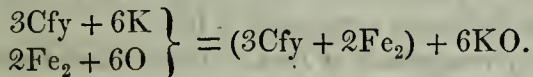
Ferrocyanide of potassium produces white precipitates with the salts of silver, zinc, and bismuth, a greenish-white with those of nickel, and green with cobalt; but the latter, by taking up water, become reddish-grey; with salts of protoxide of manganese a white precipitate is first formed, but it afterwards acquires the colour of peach-blossoms.

Sesqui-ferrocyanide of Iron.—Discovered by Diesbach in Berlin in 1710, from which it became generally known as Prussian or Berlin blue. It is formed whenever a salt of peroxide of iron is added to a soluble metallic ferrocyanide; compounds similar in colour, and probably identical in constitution, may be obtained by precipitating the ferrid-cyanide of potassium by a salt of the protoxide of iron, or by precipitating the ferrocyanide of potassium by a proto-salt of iron, adding an acid, and exposing the precipitate to the air until it becomes blue.

Prep.—By precipitating a solution of perchloride or permanganate of iron by ferrocyanide of potassium, care being taken to avoid an excess of the latter; or, by dissolving 6 parts of green vitriol and 6 parts of ferrocyanide of potassium, each by itself, in 15 parts of water, mixing the two solutions, and then adding to them 1 part of concentrated sulphuric acid and 24 parts of fuming hydrochloric acid under constant stirring. After some hours the whole should be treated with a clear solution of 1 part of bleaching powder in 80 of water, added in successive portions, care being taken to stop the addition of the bleaching liquid as soon as an effervescence arising from the escape of chlorine gas is observed. After standing some hours, the precipitate should be thoroughly washed and dried, either at common or high temperatures. Or the precipitate may be treated with dilute nitric acid till it is rendered of a deep blue colour. This yields the finest product. (Hochstätter.)

Prop.—Prussian blue dried at common temperatures is a light porous body of a deep velvet-blue colour; dried, on the contrary at high temperatures, it has a deep copper-red colour, but the powder is blue; it is tasteless, insoluble in water and dilute acids, and is not poisonous. The painters' Prussian blue of commerce contains variable quantities of earthy matter. When heated in close vessels, water, hydrocyanic acid, and carbonate of ammonia are evolved, and carburet of iron is the residue; it may be kindled in the air by a red-hot body, when it burns slowly to oxide of iron; it is decomposed by fuming nitric acid, but strong sulphuric acid unites with it, forming a white mass of the consistence of paste. Concentrated hydrocyanic acid deprives it of its iron, and liberates the hydro-ferrocyanic acid; sulphuretted hydrogen whitens it, but the colour returns on exposure to the air; metallic zinc and iron have a similar action. By peroxide of mercury it is decomposed into bicianide of mercury, and an insoluble mixture of oxide and cyanide of iron; by alkalis, into soluble ferrocyanides and peroxide of iron.

In reference to the composition of this compound, it appears from the experiments of Berzelius, that the weight of the iron of the ferrocyanogen is to that combined with it as 3 : 4; from this it may be concluded that its formation is owing to the decomposition of 3 eq. of ferrocyanide of potassium, and 2 eq. of peroxide of iron, into 6 eq. of a potassa salt and into Prussian blue.



Prussian blue appears, however, to contain the elements of water, which cannot be separated without the destruction of the compound. If this be the case, it differs from all other ferrocyanides, and must be considered as formed by the direct combination of hydro-ferrocyanic acid and peroxide of iron. Its formula will then be $3\text{CfyH}_2 + 2\text{Fe}_2\text{O}_3$; and the formula given above will represent the hypothetical anhydrous compound.

Prussian blue becomes white in the direct rays of the sun, and cyanogen is evolved; but in the dark it absorbs oxygen and recovers its colour. (Chevreul.) This change of colour in substances dyed with Prussian blue in solar light, arises from a peculiar decomposition; the recovery of the colour is owing to the formation of the so-called basic Prussian blue.

FERROCYANIDES WITH TWO BASIC METALS.

When concentrated solutions of the salts of baryta, strontia, lime, magnesia, protoxide of iron, protoxide of manganese, copper, &c., are added to a solution of the ferrocyanide of potassium, white bulky, frequently crystalline, precipitates are formed, which arise from the replacement of 1 eq. of potassium by 1 eq. of the other metal. Thus, for example, chloride of calcium gives, with the ferrocyanide of potassium, chloride of potassium, and the ferrocyanide of potassium and calcium, $\text{CaCl} + \text{K}_2\text{Cfy} = \text{KCl} + \left\{ \begin{smallmatrix} \text{K} \\ \text{Ca} \end{smallmatrix} \right\} \text{Cfy}$. These double ferrocyanides which contain an alkaline metal, although with difficulty, are nevertheless soluble in water; they contain water of crystallization; when dried at a high temperature they glow with a brilliant light, and cyanate of potassa is formed. (Campbell.)

Ferrocyanide of Potassium and Iron.—This compound is obtained in the form of a bluish-white precipitate when a salt of the protoxide of iron is added to a solution of the ferrocyanide of potassium. By the action of chlorine or nitric acid 3 eq. of potassium and 1 eq. of iron are removed from 3 eq. of the compound; Prussian blue is left. Exposed to the air it absorbs oxygen, and becomes blue; when washed, the ferrocyanide of potassium is dissolved, and after all soluble salts are removed the following compound is left.

Basic Sesqui-ferrocyanide of Iron.—By continued washing the preceding salt dissolves, without leaving any residue of oxide of iron, to a beautiful deep blue solution, which may be again evaporated to dryness without decomposition. The addition of any salt causes the separation of the compound; the precipitate may be redissolved in pure water, and is not thrown down by alcohol. Two eq. ferrocyanide of potassium and iron contain 1 eq. of ferrocyanide of potassium and 3 eq. of ferrocyanide of iron ($6\text{Fe} + 3\text{Cfy}$); of the 6 eq. of iron, 2 are converted into peroxide by the absorption of oxygen, and the ferrocyanide of potassium is dissolved; so that the soluble blue compound must be represented by the formula $\left\{ \begin{smallmatrix} 2\text{Fe}_2 \\ \text{Fe}_2\text{O}_3 \end{smallmatrix} \right\} + 3\text{Cfy}$, which corresponds to a compound of 1 eq. of Prussian blue and 1 eq. of peroxide of iron. The formation of this soluble salt is prevented by the presence of a strong acid, which unites with the peroxide of iron, and Prussian blue is left.

Ferrocyanide of Potassium with Sesqui-ferrocyanide of Iron.—The blue precipitate which falls when a salt of the peroxide of iron is

HYDRO-FERRIDCYANIC ACID.

Prepared by decomposing recently precipitated ferridcyanide of lead by the careful addition of dilute sulphuric acid; by filtration a clear yellow solution is obtained, which by careful spontaneous evaporation deposits crystals of a harsh acid taste; but, if heat be used, a deep brown powder is left. The solution readily decomposes on being kept for some time, and a blue crystalline powder is deposited; this change is promoted by heat.

Its formula is $\text{Cfdy} + \text{H}_3$; eq. = 217.34.

HYDRO-FERRIDCYANIC ACID AND METALLIC OXIDES.

This acid unites with metallic oxides, forming water and a metallic ferridcyanide; of these the compounds with the metals of the alkalies and alkaline earths, as also that corresponding to the peroxide of iron, are soluble in water; all others are insoluble in water. The latter may be prepared by the mutual decomposition of a soluble ferridcyanide and the corresponding metallic salt.

Ferridcyanide of Potassium.—Discovered by L. Gmelin. Prepared by passing a stream of chlorine gas through a solution of ferrocyanide of potassium, until it no longer gives a blue precipitate with salts of the peroxide of iron; the solution is then evaporated, and the crystals obtained by cooling purified from the admixture of chloride of potassium by re-crystallization. Its formation is owing to the decomposition of 2 eq. of ferrocyanide of potassium, $\text{Cfy}_2 + \text{K}_4$, by 1 eq. of chlorine into 1 eq. of ferridcyanide, $\text{Cfdy} + \text{K}_3 = (\text{Cfy}_2\text{K}_3)$, and 1 eq. of chloride of potassium, KCl .

Prop.—Transparent right rhombic prisms of a red colour and high lustre, are anhydrous, permanent in the air, and soluble in 3.8 parts of cold, but more freely in hot water; the solution being green, the crystals burn when held in the flame of a candle with brilliant scintillations; heated in close vessels, cyanogen and nitrogen gases are evolved, a mixture of carburet of iron and ferrocyanide of potassium is the residuc. The aqueous solution is decomposed by hydrochloric or hydrosulphuric acid; in the last case, sulphur and cyanide of iron are precipitated, and ferrocyanide of potassium and prussic acid are formed. It is one of the most delicate tests for the protoxide of iron, with which it forms a precipitate of Prussian blue; peroxide of iron is not precipitated. The solution of the red ferridcyanide precipitates most of the solutions of the heavy metals, and some of the precipitates are characteristic.

This salt may be viewed as ferrocyanide of potassium, *plus* a certain amount of ferrocyanogen, for 2 eq. of ferridcyanide $2(\text{CfdyK}_3) = 3(\text{CfyK}_2) + \text{Cfy}$.

Formula, K_3Cfdy ; eq. = 331.79.

Hydro-ferridcyanic Acid and Protoxide of Iron.—When ferridcyanide of potassium is added to a salt of protoxide of iron, there is formed a very beautiful Prussian blue, which was until lately believed to be different from that already described, and to have the formula $\text{Cfdy} + \text{Fe}_3$, the 3 eq. of potassium of the ferridcyanide being simply replaced by 3 eq. of iron. But Liebig, who has studied the reaction, has shown that it is not so simple as this, and that the blue precipitate is the same as the Prussian blue already mentioned, while yellow ferrocyanide of potassium is found in the solution, along with a salt of potash. The reaction, in the case of sulphate of potash, is as follows; it being remembered that $\text{Cfdy} = 2\text{Cfy}$, and that consequently the red salt CfdyK_3 may be represented as Cfy_2K_3 :— $2(\text{Cfy}_2\text{K}_3) + 4(\text{FeO}, \text{SO}_3) = (\text{Cfy}_3\text{Fe}_4) + (\text{CfyK}_2) + 4(\text{KO}, \text{SO}_3)$; Cfy_3Fe_4 is Prussian blue, and CfyK_2 is yellow ferrocyanide of potassium.

COBALTO-CYANIDES.

Discovered by L. Gmelin. The cyanuret of cobalt corresponding to the sesqui-oxide Co_2O_3 has not yet been obtained; united with 3 eq. of hydrocyanic acid, it forms the hydro-cobalto-cyanic acid, which is analogous to the hydro-ferridcyanic acid. This acid in its anhydrous state consists of 6 eq. cyanogen, 2 eq. cobalt, and 3 eq. hydrogen; it is a tribasic acid. The symbol of 1 eq. of its radical is Cky ; its compounds are as follow:—

$\text{Cky} = \text{Cy}_6\text{Co}_2$	= Radical Cobalto-cyanogen.
$\text{Cky} + \text{H}_3$	= Hydro-cobalto-cyanic Acid.
$\text{Cky} + \text{K}_3$	= Cobalto-cyanide of Potassium.
$\text{Cky} + \text{Pb}_3$	= Cobalto-cyanide of Lead.
$\text{Cky} + \text{Ag}_3$	= Cobalto-cyanide of Silver.

HYDRO-COBALTO-CYANIC ACID.

Prep.—The cobalto cyanide of lead is decomposed by sulphuretted hydrogen, and the clear solution, when separated by filtration from the sulphuret of lead, evaporated and allowed to crystallize.

Prop.—Colourless fibrous crystals, of a strong acid taste, deliquescent in a moist air and very soluble in water; the solution decomposes the carbonates with effervescence, and may be boiled and evaporated without change. At a higher temperature, the crystals lose first water and then hydrocyanic acid; a blue residue is left, which at a red heat burns into oxide (Zwenger).

Its formula is $\text{Cky} + 3\text{H}$; $\text{eq.} = 220.34$.

Cobalto-cyanide of Potassium.—Discovered by L. Gmelin.

Prep.—The carbonate of pure protoxide of cobalt, or the proto-cyanide, is gently heated till perfectly dissolved in a caustic solution of potassa, which has been treated with an excess of hydrocyanic acid; the solution evaporated to crystallization, and the crop of reddish-yellow crystals purified by a second crystallization.

Prop.—It crystallizes in nearly colourless or slightly yellow oblique prisms of the same form as the ferridcyanide of potassium; they are anhydrous and fuse to a green fluid. It is more soluble in hot than in cold water; the solution is colourless, without action on vegetable colours; is not decomposed by the hydrochloric, nitric, or sulphuric acids; does not precipitate the salts of iron, but forms a rose-coloured precipitate with those of the protoxide of cobalt.

Its formula is $3\text{K} + \text{Cky}$; $\text{eq.} = 334.79$.

Cobalto-cyanide of Lead.—The cobalto-cyanide of potassium causes a slight white precipitate with a solution of acetate of lead, but, by the addition of ammonia, the precipitation is rendered complete. It forms a white granular powder.

Cobalto-cyanide of Silver.—Prepared by mixing the nitrate of silver with the cobalto-cyanide of potassium. It is a white crystalline precipitate, and is soluble in ammonia, with which it forms, by the aid of heat, a double compound, crystallizable in colourless transparent prisms.

CONSTITUTION OF THE FERROCYANIDES ACCORDING TO BERZELIUS.

According to Berzelius, the cyanides form, by uniting with each other, double compounds similar to the double salts, which are produced by the oxacids; in these compounds, therefore, 1 eq. of cyanide of iron is united with 2 eq. of another cyanide, the constitution being such, if the metals be considered united with oxygen, as would be expressed by saying that the oxygen in the protoxide of iron is equal to one-half that in the other metallic oxides. Accordingly, if

Cyanide of Iron	$= \text{FeCy.}$
Hydro-ferrocyanic Acid	$= \text{FeCy} + 2\text{HCy.}$
Ferrocyanide of Potassium	$= \text{FeCy} + 2\text{KCy.}$
Ferrocyanide of Pot. and Calcium	$= \text{FeCy, } 2\text{KCy} + \text{FeCy, } 2\text{CaCy.}$
Prussian Blue	$= 2\text{Fe}_2\text{Cy}_3 + 3\text{FeCy.}$
Basic Prussian Blue	$= 2\text{Fe}_2\text{Cy}_3 + 3\text{FeCy} + \text{Fe}_2\text{O}_3.$
Soluble Prussian Blue	$= \text{KCy. FeCy} + 2\text{Fe}_2\text{Cy}_3. 3\text{FeCy.}$

CONSTITUTION OF FERRIDCYANIDES AND COBALTO-CYANIDES
ACCORDING TO BERZELIUS.

These compounds are, according to Berzelius, double cyanides, in which one eq. of sesqui-cyanide of iron or cobalt, analogous in its constitution to the peroxide of iron or cobalt, is united with 3 eq. of another cyanide.

Hydro-ferridcyanic Acid is	$\text{Fe}_2\text{Cy}_3 + 3\text{HCy}.$
Ferridcyanide of Potassium	$\text{Fe}_2\text{Cy}_3 + 3\text{KCy}.$
Ferridcyanide of Iron	$\text{Fe}_2\text{Cy}_3 + 3\text{FeCy}.$
Hydro-cobalto-cyanic Acid	$\text{Co}_2\text{Cy}_3 + 3\text{HCy}.$
Cobalto-cyanide of Potassium	$\text{Co}_2\text{Cy}_3 + 3\text{KCy}.$

Should the view adopted in this work, although opposed to the opinions of Berzelius, be hereafter shewn not to represent the real constitution of these salts, the simplicity in the formulæ, which facilitates their study, particularly in lectures, must nevertheless be considered as a beneficial change.

CONSTITUTION OF THE FERROCYANIDES ACCORDING TO
GRAHAM.

The ferrocyanides are formed from a peculiar acid, the eq. of which is triple of that of the hydrocyanic acid ; it contains 3 eq. of cyanogen, which constitutes a radical called prussine in combination with 3 eq. of hydrogen. This acid is accordingly a tribasic hydracid corresponding to the cyanuric acid ; in uniting with a metallic oxide 3 eq. of hydrogen are replaced by their eq. of the metals.

3Cy	.	.	= Pr.	Prussine.
Hydro-prussic Acid	.	.	= Pr+3H.	
Acid Hydro-prusside of Iron	.	.	= Pr+ $\left\{ \begin{array}{c} 2\text{H} \\ \text{Fe} \end{array} \right\}$	Hydro-ferrocyanic Acid.
Prusside of Iron and Potassium	.	.	= Pr+ $\left\{ \begin{array}{c} 2\text{K} \\ \text{Fe} \end{array} \right\}$	Ferrocyanuret of Potassium.
Prusside of Iron, Potassium, and Calcium	.	.	= Pr+ $\left\{ \begin{array}{c} \text{K} \\ \text{Ca} \\ \text{Fe} \end{array} \right\}$	Mosander's Salts.
Prussian Blue	.	.	= 3Pr+ $\left\{ \begin{array}{c} 3\text{Fe} \\ 2\text{Fe}_2 \end{array} \right\}$	or $\text{PrFe}_3 + 2\text{PrFe}_2.$

This view of the constitution of the ferrocyanides would have the preference to all others, could it offer any explanation why the iron in the ferrocyanide of potassium, for example, cannot be replaced by other metals, which must be the case if it be present as a basic element ; in the present state of our knowledge of these double salts it appears, nevertheless, more comprehensive than the views of Berzelius.

CHROMOCYANOGEN AND CHROMOCYANIDES.

The radical chromocyanogen is little known. Its formula is $Cy_6Cr_2 = Cry$, analogous to that of ferridcyanogen; and it forms with hydrogen the acid $CryH_3$, and with potassium the salt $CryK_3$, which forms yellow crystals, and precipitates most metallic solutions.

PLATINOCYANOGEN AND PLATINOCYANIDES.

This radical is supposed to be $Cy_2Pt = Cpy$, and to be monobasic, forming with hydrogen the acid $CpyH$, and with potassium the salt $CpyK$. The latter salt is very easily obtained by heating dried ferrocyanide of potassium gently with half its weight of spongy platinum, or still better, as Gregory recommends, with the platinum black, so as just to produce a pasty fusion. Warm water dissolves, from the dark residue, the new salt, which instantly crystallizes on cooling, so as to cause the liquid nearly to solidify. The crystals are long prisms of great beauty, exhibiting a very singular play of colour, being sulphur-yellow by transmitted, and pale blue by reflected light.

When this salt acts on protonitrate of mercury, it yields a cobalt blue precipitate, which, when heated in the liquid, becomes white, and is then platinocyanide of mercury. This salt, decomposed by sulphuretted hydrogen, yields a solution of the hydroplatinocyanic acid, which on evaporation yields crystals of a bright metallic lustre, and a colour like that of gold or copper. It is a powerful acid, and forms platinocyanides with the bases, which are all crystallisable, and in general exhibit metallic lustre by reflected light.

When chlorine is passed through a warm concentrated solution of platinocyanide of potassium, the liquid on cooling becomes nearly solid from the separation of a salt in small crystals of the aspect of burnished copper. They are either a double salt $2KCy + Pt_2Cy_3 + 5HO$, containing therefore sesquicyanide of platinum, and cyanide of potassium, or the hydrated potassium salt of a new bibasic radical Pt_2Cy_5 , with the formula $Pt_2Cy_5, K_2 + 5HO$. This is one of the most beautiful as well as one of the most remarkable salts known to chemists.

IRIDIOCYANOGEN.

This radical appears to correspond to ferrocyanogen, and to be bibasic, $Cy_3Ir = Ciy$. Its acid is obtained by the action of sulphuretted hydrogen on the lead salt, Ciy_3Pb_2 , and its formula is $CiyH_2$. The

potassium salt CiyK_2 forms colourless crystals, and its solution strikes a deep blue with salts of peroxide of iron.

PALLADIOCYANOGEN.

This radical appears to correspond to platinocyanogen, and to be formed of $\text{Pd} + \text{Cy}_2 = \text{Cpdy}$. Its potassium salt is CpdyK .

MANGANOCYANOGEN.

This radical appears to be analogous to ferridcyanogen, and to contain $\text{Cy}_6 + \text{Mn}_2 = \text{Cmy}$. Its acid will be CmyH_3 , and its potassium salt CmyK_3 . But this as well as the three preceding compounds have been merely indicated, and not fully studied.

The preceding pages exhibit a certain number of compound radicals, containing cyanogen with metals, which may be divided into three families.

1. Monobasic. Cy_2M .	
Platinocyanogen	$\text{Cpy} = \text{Cy}_2 + \text{Pt}$.
Palladiocyanogen	$\text{Cpdy} = \text{Cy}_2 + \text{Pd}$.
2. Bibasic. Cy_3M .	
Ferrocyanogen	$\text{Cfy} = \text{Cy}_3\text{Fe}$.
Iridiocyanogen	$\text{Ciy} = \text{Cy}_3\text{Ir}$.
3. Tribasic. Cy_6M_2 .	
Ferridcyanogen	$\text{Cfdy} = \text{Cy}_6\text{Fe}_2$.
Cobaltocyanogen	$\text{Cky} = \text{Cy}_6\text{Co}_2$.
Chromocyanogen	$\text{Cry} = \text{Cy}_6\text{Cr}_2$.
Manganocyanogen	$\text{Cmy} = \text{Cy}_6\text{Mn}_2$.

This view of their composition and of their salts, the general formulæ for which, including the hydrogen acids, are

Monobasic. $\text{Cy}_2\text{M} + \Delta$.	
Platinocyanides	$\text{Cpy}\Delta$.
Palladiocyanides	$\text{Cpdy}\Delta$.
Bibasic. $\text{Cy}_3\text{M} + \Delta_2$.	
Iridiocyanides	$\text{Ciy}\Delta_2$.
Ferrocyanides	$\text{Cfy}\Delta_2$.
Tribasic. $\text{Cy}_6\text{M}_2 + \Delta_3$.	
Ferridcyanides	$\text{Cfdy}\Delta_3$.
Cobaltocyanides	$\text{Cky}\Delta_3$.
Chromocyanides	$\text{Cry}\Delta_3$.
Manganocyanides	$\text{Cmy}\Delta_3$.

appears both simple and more easily retained than any other, and agrees with all the known facts.

Against the view of Berzelius, which, as above explained, considers the salts as double cyanides, it may be argued that in that case they must contain either hydrocyanic acid or cyanide of potassium, as in the

formulæ $2\text{KCy} + \text{FeCy}$ for ferrocyanide of potassium, and $3\text{HCy} + \text{Fe}_2\text{Cy}_3$ for hydroferridcyanic acid. Now both these compounds, hydrocyanic acid and cyanide of potassium, are not only very poisonous, but very easily decomposed; but, on the contrary, the whole series of salts and acids here described are quite inert, and very permanent. Moreover, we are acquainted with many double cyanides which have the characters we should expect in such compounds. Liebig's view is, therefore, here preferred.

CHLORIDE OF CYANOGEN.

Two compounds of chlorine with cyanogen are known, and these are isomeric in their constitution. The one, which at common temperatures is gaseous, was discovered by Gay-Lussac; the other, which is a crystalline solid, by Serullas.

Gaseous Chloride of Cyanogen.—Is formed when chlorine gas is transmitted into hydrated prussic acid, when moist bicyanide of mercury is placed in an atmosphere of chlorine in the dark, or when mellone is heated in dry chlorine gas. This compound, which is gaseous at common temperatures, has a most powerful penetrating odour, excites the eyes to a copious flow of tears, becomes solid at 0° , and forms long acicular needles, which fuse at 5° and boil at 10° ; but, under a pressure of four atmospheres, it is still liquid at 70° . If the liquid be introduced into glass tubes and hermetically sealed, it is gradually converted into the solid chloride, and regular crystals of the following compound are obtained:—Water dissolves 25, alcohol 100, and ether 50 times its volume of the gas without change. It is decomposed by the alkalies; salts of the protoxide of iron are rendered of a deep green colour when an alkali is added to the mixture. If moistened bicyanide of mercury in chlorine gas be exposed to solar light, a heavy oily liquid of a yellow colour is formed, which is insoluble in water, and has the same odour as the gaseous chloride; the same substance appears to be formed by the action of chlorine upon the fulminate of silver. If it be dissolved in alcohol, and its solution thrown into water, a crystalline substance like camphor is precipitated; on exposing a mixture of moist chlorine and chloride of cyanogen gases to the sun's rays, two other solid compounds appear to be formed. The probable formula of this gas is CyCl .

Solid Chloride of Cyanogen.—Discovered by Serullas. It is formed by exposing dry chlorine gas and anhydrous hydrocyanic acid to the sun's light; hydrochloric acid and the solid chloride, which is deposited in crystals, are formed. It may also be formed by heating sulpho-

cyanide of potassium in a stream of dry chlorine gas. In the pure state it is white, sublimes in long transparent crystals, has a penetrating odour similar to the excrement of mice, and a sweet biting taste; its sp. gr. = 1.32; fuses at 284° , sublimes at 374° . By digestion in water at a gentle heat, it is decomposed into cyanuric and hydrochloric acids, from which its constitution must be represented by the formula Cy_3Cl_3 . It is soluble in absolute alcohol and ether without decomposition.

With dry ammoniacal gas, a white compound, containing chlorine, which is not decomposed by water, and sal-ammoniac are formed; its constitution is very imperfectly known.

From the circumstance, that the density of the vapour of the solid chloride is three times that of the gaseous chloride, and that the latter, when decomposed by water, yields hydrochloric and cyanic acids, while the former, under the same circumstances, gives rise to hydrochloric and cyanuric acids, we are justified in concluding that the formula of the gaseous compound is $CyCl$, while that of the solid is Cy_3Cl_3 . Moreover, referring to the facts formerly mentioned as to the existence of allotropic modifications of sulphur, phosphorus, and carbon, it appears highly probable that the cyanogen in the two compounds exists in two different allotropic conditions, the one being C_2N_4 , the other C_6N_8 , (possibly paracyanogen, see that compound). If so, then we can easily see how the one should give rise to CyO , and $CyCl$, and the other to Cy_3O_3 and Cy_3Cl_3 , and we may also conjecture that fulminic acid, Cy_2O_2 , contains a third modification, the chloride of which is not yet known. In this point of view a careful study of these and of other analogous compounds is of high importance, and could hardly fail to yield very interesting results.

BROMIDE OF CYANOGEN.

This compound is readily obtained by bringing together in a retort two parts of bichloride of mercury and one of bromine, by the mixture of which a powerful heat is developed. By applying a gentle heat as soon as the first action is over, the bromide of cyanogen passes over and fills the neck of the retort in the form of white cubic crystals, which are exceedingly volatile, are gaseous at 60° , and are very soluble in water and alcohol. This compound possesses an exceedingly powerful irritating odour, and is very poisonous. Its formula is $CyBr$.

IODIDE OF CYANOGEN.

Formed by heating dry cyanide of mercury or silver with iodine (Wöhler): most conveniently by heating a mixture of bicyanide of mercury, iodine, and water, in a retort (Mitscherlich); when at a gentle temperature the iodide sublimes, and collects in the neck of the retort as a fine crystalline snow, or in long needles. The crystals have a penetrating odour, which excites a flow of tears, may be dissolved in alcohol, ether, and water without decomposition, and are perfectly volatilized at 100° . Its formula is CyI .

CYANOGEN AND SULPHUR.

Sulpho-cyanogen, Bisulphuret of Cyanogen.—Unknown in the separate state. When a concentrated solution of a metallic sulphocyanide is saturated with chlorine, or heated with nitric acid, a deep orange-yellow, amorphous powder is formed, which retains its colour when dry; is light, porous; is insoluble in water, alcohol, and ether, but is dissolved by strong sulphuric acid from which it is precipitated by water. The recent researches of Jamieson have shewn that this orange powder, when purified by boiling with water as long as any thing is dissolved, is a uniform and definite compound of sulphocyanogen CyS_2 , with 1 eq. hydrosulphocyanic acid CyS_2H , and 1 eq. water HO ; in all, $\text{Cy}_2\text{S}_4\text{H}_2\text{O}$, or $\text{C}_4\text{N}_2\text{S}_4\text{H}_2\text{O}$. It is decomposed by nitric acid and by potassium with the aid of heat, giving rise to the formation of the sulphuret, cyanide, and sulphocyanide of potassium; suffers decompositions, which have been but slightly studied, by the action of the alkalis and soluble metallic sulphurets, and is dissolved readily and completely in hydrosulphate of sulphuret of potassium with the evolution of hydrosulphuric acid; from this solution acids throw down a new substance in the form of a white or yellowish-white precipitate, which Jamieson has found to be the hydrogen acid of a new compound radical *sulpho-mellone*. The decomposition of the yellow powder by the action of heat is peculiarly remarkable, the products of its destructive distillation being sulphuret of carbon, sulphur, and the residue mellone, which at a high temperature is decomposed into nitrogen and cyanogen gases. From 4 eq. sulphocyanogen, 2 eq. bisulphuret of carbon, 4 eq. sulphur, and a residue of 1 eq. mellone, C_6N_4 are obtained. (See Products of the Decomposition of Sulpho-cyanogen.)

Lassaigne has described in the *Ann. de Ch. et Ph.* xxxix., as a new compound of cyanogen and sulphur, a substance which he obtained by the action of the perchloride of sulphur upon the bicyanuret of mer-

cury; it occurred as brilliant colourless crystals, which are powerful refractors of light, have a strong penetrating odour, and cause a flow of tears. This substance contains chlorine, the quantity of which has not been determined, 24 per cent. of sulphur and cyanogen; it is dissolved, and at the same time decomposed, by water, and the solution reddens the salts of the peroxide of iron. It is probable that this reputed compound of 2 eq. of cyanogen and 1 eq. sulphur is nothing more than a double compound of the chlorides of cyanogen and sulphur.

Formula, $Cy + 2S$; symb. = Csy ; eq. = 58.59.

HYDRO-SULPHOCYANIC ACID.

Discovered by Rink. Occurs in the seeds and blossoms of the Cruciferæ (Sinapis, &c.), and in the saliva of man and sheep.

Prep.—By decomposing the basic sulphocyanide of lead by dilute sulphuric acid, care being taken to leave some lead in the solution, which is afterwards separated by sulphuretted hydrogen; or by decomposing sulphocyanide of silver suspended in 10 volumes of water by sulphuretted hydrogen.

Prop.—A colourless fluid of a pure acid taste, which by the action of the air, and on being heated, readily decomposes into a variety of products; one of these deposits itself from the acid as a lemon-yellow, insoluble powder. It cannot exist without water. On treating the aqueous acid with chlorine or nitric acid, it is deprived of hydrogen, and the orange powder above mentioned is precipitated: by a further action cyanic and sulphuric acids are formed, but the former is at once decomposed into carbonic acid and ammonia. It colours the salts of peroxide of iron blood-red, and is not poisonous.

Formula = $Csy + H$; eq. = 59.59.

HYDRO-SULPHOCYANIC ACID AND AMMONIA.

Sulphocyanide of Ammonium.—By saturating the acid with ammonia and gently evaporating, a semi-fluid saline mass is obtained, which, at a higher temperature, suffers a peculiar decomposition. At first ammoniacal gas is evolved, then sulphuret of carbon, and at last the protosulphuret of ammonia is sublimed. The residue, when the heat has not been pushed too far, consists of melam, or of a mixture of melam with mellone.

Sulphocyanide of ammonium is also formed by adding sulphuret of carbon to alcohol, which has been saturated with ammonia.

Formula = $NH_4 + CyS_2$; eq. = 75.74.

METALLIC SULPHOCYANIDES.

The hydro-sulphocyanic acid must be considered as a compound analogous in its constitution to the hydrated cyanic acid, the oxygen of the latter having been replaced by its equivalent of sulphur. Considered as a hydracid, the formula of the hydrated cyanic acid would be $\text{CyO}_2 + \text{H}$, corresponding to that of the hydro-sulphocyanic acid, $\text{CyS}_2 + \text{H}$.

On its being brought into contact with the metallic oxides, the hydrogen is replaced by 1 eq. of the metal. The soluble metallic sulphocyanides may be formed:—by the action of the acid on the metallic oxide, by heating the higher sulphurets of the alkaline metals to redness in cyanogen gas, or by conducting cyanogen gas into their solution, by heating or fusing the soluble metallic cyanides with sulphur, or the insoluble cyanides with the soluble sulphuret.

The soluble metallic sulphocyanides colour the salts of peroxide of iron blood-red; are decomposed, when heated in dry hydrochloric acid gas, into metallic chlorides and anhydrous hydro-sulphocyanic acid, but the latter instantly decomposes into other products. The sulphocyanides of the alkaline metals, when dry, bear a strong heat without decomposition, but if oxygen be present, they are converted, with the evolution of sulphurous acid, into salts of cyanic and sulphuric acids; those of the heavy metals are decomposed by the red heat into mixtures of metallic sulphurets and mellone, this change being generally accompanied by the evolution of sulphuret of carbon and sulphur; at a higher temperature the residue evolves cyanogen and nitrogen gases in the proportion of 3 : 1. Heated to redness in chlorine gas, they give rise to metallic chlorides, mellone, chlorides of sulphur and cyanogen, and a small quantity of the sulphuret sublimes unchanged; they are most of them soluble in alcohol. The proto-salts of mercury are decomposed by the soluble sulphocyanides into metallic mercury which is deposited, and into the soluble bisulphocyanide. All the soluble sulphocyanides form with the bicyanide of mercury double compounds, which are readily obtained in crystals.

Sulphocyanide of Potassium.—*Prep.*—46 parts of ferrocyanide of potassium, gently roasted to drive off water of crystallization, is mixed in the form of a fine powder with 32 parts of flowers of sulphur, and 17 of pure carbonate of potash, and the mixture fused in an iron vessel, the heat being only raised at the end of the fusion to low redness. The mass when cold is dissolved in boiling water, and the clear liquid separated from the precipitated iron by filtration. On evaporation

crystals are obtained, which are separated from the admixture of carbonate of potassa by being redissolved in alcohol. In this process, the whole cyanogen of the ferrocyanide is converted into cyanide of potassium; but as the ferrocyanide contains only 2 eq. of potassium with 3 eq. of cyanogen, the third eq. of potassium is supplied by an eq. of carbonate. The 3 eq. of cyanide of potassium then take up 6 eq. of sulphur to form the sulphocyanide, while carbonic acid and oxygen are expelled, and the iron is converted into sulphuret. $(2\text{KCy} + \text{FeCy}) + (\text{KOCO}_2) + \text{S}_7 = 3(\text{CyS}_2\text{K}) + \text{CO}_2 + \text{FeS} + \text{O}$. It is probable that part of the iron is oxidized, and part of the sulphur of the sulphuret dissipated, but the above equation accounts for the production of the sulphocyanide, which is obtained, when the operation is carefully performed, in a proportion very nearly corresponding to that indicated by the theory.

Prop.—Crystallizes in long striated colourless prisms, which are anhydrous, of a cooling, somewhat biting taste, fuse much below the red heat to a clear liquid; deliquesces in a moist atmosphere, very soluble in hot alcohol, from which it crystallizes on cooling.

Formula, KCsy ; eq.=97.74.

Sulphocyanide of Lead.—Prepared by mixing concentrated solutions of acetate of lead and sulphocyanide of potassium. Forms yellow opaque crystals of a strong lustre, which are decomposed by boiling in water into hydro-sulphocyanic acid and a basic sulphocyanide. Formula is $\text{Csy} + \text{Pb}$. The basic salt is formed by mixing a solution of sulphocyanide of potassium with subacetate of lead; it is a yellowish-white crystalline insoluble powder.

Its formula is $\text{Csy}, \text{Pb} + \text{PbO}$.

Sulphocyanide of Copper.—Prepared by adding a solution of protosulphate of iron to a mixture of sulphate of copper and sulphocyanide of potassium. It falls as a white granular precipitate, which is insoluble in water.

Formula, $\text{Csy} + \text{Cu}$.

Sulphocyanide of Silver.—Prepared by precipitating the neutral nitrate of silver by sulphocyanide of potassium. A white curdy precipitate, insoluble in water, but dissolved by ammonia, from which it crystallizes in brilliant white plates.

PRODUCTS OF THE DECOMPOSITION OF CYANOGEN AND ITS COMPOUNDS.

CYANOGEN AND WATER.

A solution of cyanogen in water acquires rapidly in the light, but more slowly in the dark, a brown colour, and a brown flocculent precipitate falls; the solution is then found to contain carbonic acid, prussic acid, ammonia, urea, and oxalate of ammonia (Wöhler); according to the analyses of Pelouze and Richardson, the composition of the brown material may be expressed by $\text{NC}_2 + \text{HO}$, which denotes a compound of 1 eq. cyanogen and 1 eq. of water; but it is considered by others to be the result of the action of 2 eq. cyanogen on 4 eq. water, and to be produced with ammonia, which it retains; thus, $2(\text{C}_2\text{N}) + 4(\text{HO}) = \text{NH}_3 + \text{C}_4\text{HNO}_4$. This last formula differs from the preceding by $\text{C}_2\text{O}_3 + \text{NH}_3$. According to others, again, it contains the elements of 2 eq. cyanogen and 1 eq. of water, and is $\text{C}_4\text{N}_2\text{HO} = \text{Cy}_2 + \text{HO}$, containing no ammonia. It is readily dissolved by alkalies and acetic acid, but forms with the oxides of the heavy metals insoluble compounds. At a red heat paracyanogen is formed.

The different products, which arise from the reaction of cyanogen and water, are without doubt the results of several perfectly independent decompositions. One eq. of cyanogen and 3 eq. water contain the elements of 1 eq. of anhydrous oxalate of ammonia; 2 eq. cyanogen and 1 eq. water, the elements of 1 eq. of cyanic and 1 eq. of hydrocyanic acid. One eq. of hydrocyanic acid, in the presence of oxalic acid, or of ammonia, is resolved with 4 eq. of water, into formic acid and ammonia, $\text{C}_2\text{HN} + 4\text{HO} = \text{NH}_3, \text{HO} + \text{C}_2\text{HO}_3$. Carbonate of ammonia is formed from the decomposition of cyanic acid, and three equivalents of water; urea, by the union of cyanic acid with ammonia and water.

This remarkable decomposition, in which two binary compounds, cyanogen and water, give rise to so many ternary and quaternary compounds, is a very instructive example of the spontaneous transformation which is called putrefaction. Not less than eleven or twelve new compounds are, or may be, formed. These are, 1, the black solid; 2, ammonia; 3, cyanic acid; 4, hydrocyanic acid; 5, oxalic acid; 6, carbonic acid; 7, a second brown solid, containing paracyanogen; 8, formic acid; 9, formate of ammonia; 10, oxalate of ammonia; 11, bicarbonate of ammonia; 12, urea.

CYANOGEN AND AMMONIA.

If cyanogen gas be conducted into liquid ammonia, a decomposition similar to that produced by water ensues, but in a much shorter time. A large quantity of a brown substance, which contains ammonia in chemical combination, is deposited; the soluble products are as above. According to Johnston, the composition of this brown substance may be represented by the formula $C_6N_4H_6O_4$ or $C_6N_3O + NH_3 + H_3O_3$, consequently as a hydrated ammoniacal compound of an acid, which contains the same quantity of cyanogen as the cyanuric acid, and may therefore be considered as the protoxide of the radical of the latter acid.

By heating this brown precipitate to redness, paracyanogen, water, and carbonate of ammonia are obtained; this decomposition is readily explained, when it is recollected that this product may be considered as a compound of cyanogen (C_4N_2) with ammonia and cyanic acid; the latter of which, by decomposing with 3 eq. water, forms 2 eq. of carbonic acid and 1 eq. of ammonia.

PARACYANOGEN.

Discovered by Johnston. Formed by heating to redness the brown precipitate formed by the decomposition of cyanogen with water or ammonia; left in small quantity on decomposing bicianuret of mercury in a retort by heat. A dark brown powder, insoluble in water; when burnt with oxide of copper it evolves nitrogen and carbonic acid gases in the proportion of 1 : 2 by volume. Is dissolved by concentrated sulphuric acid; dissolved with decomposition by nitric acid; the addition of water renders the solution turbid, and a yellow precipitate falls, the paracyanic acid (Johnston), the properties and constitution of which require an accurate investigation. According to Johnston, whose experiments on this point have been confirmed by Liebig and Gregory, the composition of paracyanogen in 100 parts is the same as that of cyanogen. Its formula, as deduced by Johnston from some of its compounds, is $C_6N_3=3C_2N$. Should this prove to be the case, it may probably be the radical of cyanuric acid and of the solid chloride of cyanogen. But it must be considered still doubtful whether paracyanogen be a pure definite compound, or a mixture of mellone, C_6N_4 with carbon in uniform proportions.

PRODUCTS OF THE DECOMPOSITION OF SULPHO-CYANOGEN.

MELLONE.

A compound radical; discovered by Liebig. When dry sulphocyanogen, or rather the yellow powder which contains it, is heated in a retort to redness, it is decomposed into sulphuret of carbon, sulphur, and mellone; 4 eq. sulphocyanogen, $C_8N_4S_8$, yield 4 eq. sulphur S_4 , 2 eq. bisulphuret of carbon C_2S_4 , and 1 eq. mellone C_6N_4 . This substance is also left mixed with chloride of potassium by the decomposition of sulphocyanide of potassium in chlorine gas; also by exposing melam, ameline, and ammelide to a red heat.

Prop.—A lemon-yellow powder, insoluble in water, alcohol, and dilute hydrochloric and sulphuric acids, but soluble with decomposition in nitric acid and the caustic fixed alkalies; is decomposed by a strong red heat into 3 volumes cyanogen and 1 volume of nitrogen gas; unites directly with potassium with the production of light to the mellonide of potassium, with hydrogen, indirectly, to hydromellonic acid; decomposes the iodide, bromide, and sulphocyanide of potassium, on being fused with them, with the evolution of iodine, bromine, and sulphocyanogen. Its compounds with the other metals are not known.

Its formula is C_6N_4 ; eq.=93.32.

HYDROMELLONIC ACID.

Discovered by L. Gmelin. Prepared by dissolving mellonide of potassium in boiling water, and adding to the solution hydrochloric, sulphuric, or nitric acid. A dirty white gelatinous precipitate, which dries to a yellow powder, the hydrated hydromellonic acid. It is slightly soluble in cold, more freely in hot water, has a slightly acid reaction, and is not decomposed by hydrochloric and nitric acids. It is remarkable for its power of resisting a low red heat, and has been on this account, and from its gelatinous aspect when precipitated, taken for silicic acid.

Formula, $C_6N_4 + H$; eq.=94.32.

HYDROMELLONIC ACID AND METALLIC OXIDES.

The hydromellonic acid is decomposed by metallic oxides into a metallic mellonide and water; it decomposes the carbonates both in the dry state and in solution, and the iodides and bromides on fusion.

Its compounds with the alkaline metallic oxides and with the earths are insoluble in water.

Mellonide of Potassium.—Prepared by fusing sulphocyanide of potassium in a porcelain crucible at a red heat, and adding mellone as long as an evolution of sulphuret of carbon and sulphur is remarked. A brown opaque glassy mass is obtained, which dissolved in boiling water yields, as the solution cools, hydrated crystals of mellonide of potassium. It is also formed as a secondary product in the process for the preparation of the sulphocyanide of potassium, especially if the heat has been too high, when the sulphocyanogen is partially decomposed, yielding mellonc. The mellone being permanent in a low red heat, seizes the potassium, and the mellonide is also very permanent. It is present in the solution in small, but in the residue in larger quantity, from which it may be removed by boiling water.

Prop.—Crystallizes from water in colourless fine needles, which unite into dense flakes; a concentrated solution congeals to a soft white mass, which is with difficulty dissolved by cold water; the crystals contain water of crystallization; which they lose at a high temperature; they then fuse without loss of weight to a clear yellow glass. The solution is tasteless, and precipitates all earthy and metallic salts.

By fusing sulphocyanide of potassium with mellone, the sulphocyanogen is liberated, and is instantly decomposed by the high temperature into sulphuret of carbon, sulphur, and mellone. By fusing ferrocyanide of potassium with sulphur, the sulphocyanide of potassium and sulphocyanide of iron are formed; 4 eq. of the latter decompose into 4 eq. sulphuret of iron 4FeS , 2 eq. sulphuret of carbon 2CS_2 , and 1 eq. of mellonc, which as soon as it is formed decomposes 1 eq. of sulphocyanide of potassium into mellonide of potassium and sulphocyanogen; the latter is further decomposed into sulphur, sulphuret of carbon, and mellonc.

Formula, $\text{K} + \text{C}_6\text{N}_4$; eq. = 132.47.

PRODUCTS OF THE DECOMPOSITION OF MELLONE.

CYANILIC ACID.

By a long-continued boiling of mellone in dilute nitric acid, a solution is effected with the evolution of gaseous products, and the liquid yields on evaporation colourless, transparent, octohedral crystals; by resolution in hot water, hydrated cyanilic acid in soft tabular crystals of a mother-of-pearl lustre are obtained. This acid has the same com-

position as the crystalline cyanuric acid ; contains, like the latter, 4 eq. water of crystallization, which it loses at 212° , when it becomes opaque and falls to a white powder. By the destructive distillation it is converted into hydrated cyanic acid ; by solution in sulphuric acid and caustic potassa into cyanuric acid. This acid has been but little examined. Its formation admits of explanation on the supposition that the elements of 1 eq. of mellone and 4 eq. of water give rise to 1 eq. cyanilic acid and 1 eq. ammonia, and the latter is in point of fact found combined with the nitric acid ; according to this, its formation ought not to be dependent on the use of nitric acid alone.

MELLONE AND POTASSA.

On boiling mellone with potassa, the former is dissolved with the evolution of ammonia, and on evaporating the solution a very soluble salt of potassa crystallizes in long needles. If the warm solution be treated with acetic acid, a compound containing potassa is precipitated in brilliant crystalline plates ; by dissolving these in nitric acid a substance is formed, which is free from potassa, and may be obtained in brilliant and transparent acicular crystals ; it gives with salts of silver a white precipitate, which contains 58.8 per cent. of silver, and is not soluble in dilute nitric acid.

HYDRO-PERSULPHOCYANIC ACID.

Product of the decomposition of hydro-sulphocyanic acid. On fusing sulphocyanide of potassium in a stream of dry hydrochloric acid gas, hydro-sulphocyanic acid is separated, but at the same time decomposes into bisulphuret of carbon, hydrocyanic acid, and a yellow substance which is insoluble in water. If this decomposition be conducted in a retort, its neck will be found coated with this yellow or red solid material in large quantity ; it is soluble in hot alcohol, from which it is deposited on cooling in the form of a pale yellow crystalline mass, which is slightly soluble in water. The composition of this substance may be represented by the formula $CyS_3 + H$, according to which it contains 1 eq. more of sulphur than the hydro-sulphocyanic acid ; it is readily dissolved by the alkalies, and forms, with the other metallic oxides, peculiar and usually insoluble compounds. (Woskresensky.)

MELAM.

A product of the decomposition of sulphocyanide of ammonium. Discovered by Liebig. When the sulphocyanide of ammonium, or a

mixture of 2 parts of sal-ammoniac and 1 of sulphocyanide of potassium are heated to the point of fusion of the latter, the sulphocyanide of ammonium is decomposed into three gaseous and one solid product. The former are ammonia, hydro-sulphuric acid, and the sulphuret of carbon; the latter is melam, which is left in the retort mixed with chloride of potassium, and is separated from it by washing with water.

Prop.—A white amorphous powder; insoluble in water, alcohol, and ether, but dissolved by hot potassa, by which a part of it is decomposed, but another portion is again deposited unchanged as the solution cools; it is also soluble in hot concentrated sulphuric and nitric acids, from which alcohol and water throw down ammelide. If the solution in these strong acids be boiled for some time, it is completely converted into cyanuric acid and ammonia; 1 eq. of melam and 12 eq. water contain the elements of 2 eq. of cyanuric acid and 5 eq. ammonia. It is dissolved in hydrochloric and dilute nitric acids and potassa with the formation of ammeline and melamine; fused with hydrate of potassa, ammonia is evolved, and cyanate of potassa produced; and with potassium the mellonide of potassium is formed. When heated, it decomposes into mellone and ammonia.

Explanations.—On heating 8 eq. of sulphocyanide of ammonium, they are decomposed into 1 eq. melam, 10 eq. ammonia, 4 eq. sulphuret of carbon, and 8 eq. hydrosulphuric acid; 1 eq. melam, on being fused with 6 eq. hydrate of potassa, gives rise, by the addition of the elements of 6 eq. of water, to 6 eq. of cyanate of potassa and 5 eq. ammonia. By a long-continued application of heat to melam in caustic potassa, it is decomposed together with 2 eq. water into 1 eq. melamine and 1 eq. ammeline. Melam is converted into ammelide by the addition of the elements of 6 eq. water, which form 1 eq. ammelide and 2 eq. ammonia. Its formula is $C_{12}N_{11}H_9$; eq. = 238.09.

MELAMINE.

A saline base; discovered by Liebig. A product of the decomposition of melam by alkalies and dilute acids.

Prep.—The residue left from the distillation of 1 part of sulphocyanide of potassium and 2 parts of sal-ammoniac (raw melam) is boiled, after the removal of the chloride of potassium, with a solution of 1 part of hydrate of potassa in 20 parts of water, till the whole is dissolved, and the solution is perfectly clear; it is then gently evaporated till brilliant crystalline scales are observed, when it is allowed to cool and the whole of the melamine is deposited; it is purified by a second crystallization.

Prop.—Crystallizes in pretty large colourless or slightly yellow rhombic octohedrons; they are transparent, anhydrous, sparingly soluble in cold, but pretty freely though slowly in boiling water, unchanged by the air, and insoluble in alcohol and ether. The aqueous solution has no action on vegetable colour, and is of a slightly bitter taste. It fuses when heated, and sublimes principally unchanged, but a small quantity is decomposed into mellon and ammonia. It is decomposed by concentrated nitric and sulphuric acid, with the aid of heat, into ammonia and ammeline or ammeline; fused with hydrate of potassa, the elements of 3 eq. of water add themselves to its constituents and form 6 eq. ammonia, which are evolved, and 3 eq. cyanate of potassa are left.

Its formula is $C_6N_6H_6$; eq. = 121.62.

MELAMINE AND ACIDS.

Melamine combines with dilute acids to crystallizable salts, all of which, with the exception of the double salts, have an acid reaction. The sulphate, nitrate, phosphate, and oxalate are less soluble than melamine itself; the acetate and formiate of melamine are very soluble; it precipitates magnesia from the hot solutions of its salts, owing to the formation of a double salt; the same occurs with all salts, the base of which is an oxide of a heavy metal. Melamine combines directly with the anhydrous hydracids; all its salts with the oxacids correspond to the ammoniacal salt in containing an equivalent of water, without which they cannot exist; it forms double basic salts, in which this equivalent of water is replaced by a metallic oxide.

AMMELINE.

A saline base; discovered by Liebig. A product of the decomposition of melam and melamine by acids and alkalis.

Prep.—The alkaline solution, from which the melamine is formed from the decomposition of melam by the caustic potassa, contains ammeline dissolved in the potassa; it is completely precipitated by neutralizing the solution with acetic acid. The white gelatinous precipitate formed is added to dilute nitric acid as long as it is dissolved, and the solution on evaporation yields crystals of pure nitrate of ammeline; this should be redissolved in very dilute nitric acid, the ammeline precipitated by carbonate of ammonia, and should be then well washed and dried. The substance may also be obtained by dissolving melam in dilute boiling hydrochloric acid, and evaporating when the hydro-

chlorates of ammeline and melamine crystallize; the crystals are to be dissolved in pure water and precipitated by ammonia. The liquid which drains from the precipitate, as well as the water used in washing, contains melamine, which by evaporation may be obtained as hydrochlorate.

Prop.—A brilliant white precipitate which consists of very fine needles of a silky lustre; it is insoluble in alcohol and ether, but dissolves in caustic alkalies, yields when distilled alone a crystalline sublimate and ammonia, with a residue of pure mellon, is soluble by acids with which it forms crystallizable salts. By long-continued boiling in dilute acids, or on being dissolved in concentrated sulphuric acid, it is decomposed by the addition of 1 eq. of water into ammonia and ammeline. By fusion with caustic potassa, 1 eq. of water is decomposed, and it is converted into ammonia and cyanate of potassa.

Its formula is $C_6N_5H_5O_2$; eq. = 128.47.

AMMELINE AND ACIDS.

Ammeline is a weak saline base, and forms only with the strong, and not with the organic acids, crystallizable salts which have an acid reaction, and are partially decomposed by water with the deposition of ammeline. By adding a solution of the nitrate of ammeline to the salts of several heavy metals, a crystalline precipitate is formed, which is a basic double salt, composed of 1 eq. of acid, 1 eq. of ammeline, and 1 eq. of metallic oxide. The salts of ammeline with the oxacids contain like the ammonia salts 1 eq. of water, without which they cannot exist; the double salts are anhydrous.

Nitrate of ammeline crystallizes in large broad plates, or in long quadrangular prisms; when heated it fuses, and ammeline is left as a residue, while nitric acid and the products of the decomposition of nitrate of ammonia are evolved.

AMMELIDE.

Discovered by Liebig. A product of the decomposition of melam, melamine, and ammeline by concentrated acids. Melam, melamine, or ammeline is dissolved in concentrated sulphuric acid, the solution mixed with alcohol, and the precipitate formed washed with cold water until all acid is removed. It may be purified by re-solution in dilute nitric acid, and precipitation by carbonate of ammonia.

Prop.—A white powder, insoluble in water, alcohol, and ether, but soluble in alkalies and strong acids, forming with the nitric acid a crys-

talline compound which is decomposed by water ; by continued boiling in dilute nitric or sulphuric acid it is entirely decomposed into cyanuric acid and ammonia.

Formula, $C_{12}N_9H_9O_6$; eq. = 257.79.

Melamine, by the action of hydrochloric acid, aided by heat, is transformed into ammeline, giving off ammonia, while water is taken up. $C_6N_6H_6 + H_2O_2 = C_6N_6H_8O_2$, and $C_6N_6H_8O_2 - NH_3 = C_6N_5H_5O_2$.

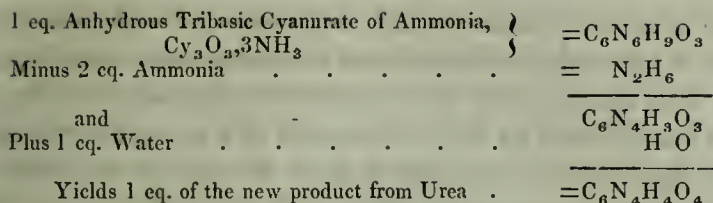
Melam also, when treated in the same way, yields ammeline and ammonia. $C_{12}N_{11}H_9 + H_4O_4 = C_{12}N_{11}H_{13}O_4$; and $C_{12}N_{11}H_{13}O_4 - NH_3 = C_{12}N_{10}H_{10}O_4 = 2(C_6N_5H_5O_2)$.

All these substances may be resolved, by the action of acids, into cyanuric acid and ammonia. It appears that they are all, that is, melam, melamine, and ammeline, first converted into ammeline, and that ammeline is the source of the cyanuric acid and ammonia.

It is obvious that they are all closely related to each other, and to cyanuric acid. That they are also related to mellone is probable, because when heated they leave a yellow residue, which is converted by a stronger heat into cyanogen and nitrogen ; which, in short, is mellone. All these compounds may be represented as tribasic cyanurate of ammonia, minus water, or ammonia, or water and ammonia. Thus,

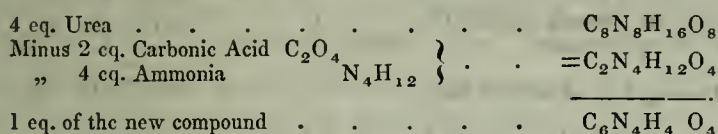
1 eq. Anhydrous Cyanurate of Ammonia, $Cy_3O_3, 3NH_3$	$= C_6 N_6 H_9 O_3$
Minus 3 eq. Water	$= H_3 O_3$
Yields 1 eq. Melamine	$= C_6 N_6 H_6$
1 eq. Anhydrous Cyanurate of Ammonia	$= C N_6 H_9 O_3$
Minus 1 eq. Water	$= HO$
„ 1 eq. Ammonia	$= H_3N$
	$\left. \begin{array}{l} NH_4O \\ NH_4O \end{array} \right\}$
Yields 1 eq. Ammeline	$= C_6 N_5 H_5 O_2$
2 eq. Anhydrous Cyanurate of Ammonia	$= C_{12} N_{12} H_{18} O_6$
Minus 1 eq. Ammonia	$= NH_3$
„ 6 eq. Water	$= H_6O_6$
Yields 1 eq. Melam	$= C_{12} N_{11} H_9$
2 eq. Anhydrous Cyanurate of Ammonia	$= C_{12} N_{12} H_{18} O_6$
Minus 3 eq. Ammonia	$= N_3 H_9$
Yields 1 eq. Ammeline	$= C_{12} N_9 H_9 O_6$

When the mass remaining in the retort when urea is heated, and formerly believed to be cyanuric acid or cyanurate of ammonia, is acted on by acids, it yields cyanuric acid, and ammonia is found in the solution ; but if it be boiled with water, an insoluble snow-white powder is obtained, which agrees with ammeline in almost all its properties. Its formula, however, is $C_6N_4H_4O_4$, and it may also be derived from cyanurate of ammonia, as follows :—



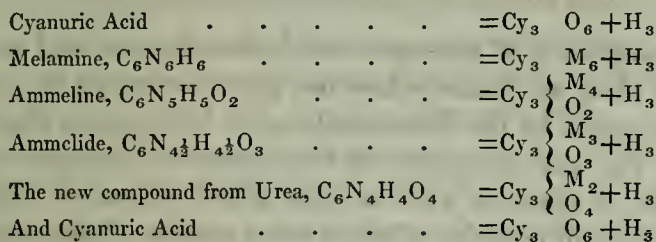
This product, therefore, is intermediate between ammeline and cyanuric acid.

To be transformed into hydrated cyanuric acid, it has only to lose 1 eq. ammonia, and to gain 2 eq. water. Its formation from urea is very easily understood; for 4 eq. urea, minus 2 eq. carbonic acid and 4 eq. ammonia, will give this compound:—



THEORY OF THE COMPOSITION OF MELAMINE, AMMELINE, AND AMMELIDE.

The following attempt has been made to give a satisfactory explanation of the basic qualities of melamine and ammeline, and of their connection with ammeline and cyanuric acid. It is assumed that these substances contain the same radical as cyanuric acid, together with a compound of nitrogen and hydrogen, which is composed of equal volumes of these elements, and which we shall suppose to be denoted by the symbol $2M=HN$; the compounds may then be represented in the following form:—



The cyanuric acid is, as may be seen, both the commencement and termination of the series; in melamine, the 6 eq. of oxygen are replaced by $6M(N_3H_3)$, and in ammeline 4 eq. by $4M$; both of them are saline bases. The ammeline has no basic properties, and in it one-half of the oxygen of the cyanuric acid is replaced by $3M$, and by the further removal of all M cyanuric acid is again produced. The basic properties of these bodies decrease as the quantity of oxygen which combines with the radical is increased. The cyanuric acid may be

may again be obtained in crystals ; soluble by alkalies in the cold, and precipitated unchanged from the solution by acids ; but on the application of heat a mixture of a metallic sulphuret and a sulphocyanide is formed ; its solution precipitates salts of silver, lead, and copper ; the compound with the first of these metals is decomposed when gently heated into sulphuret of silver and free cyanogen gas. Its formula is $Cy_3S_6H_6 + aq.$

HYDRO-SULPHOCYANIC ACID AND HYDROSULPHURIC ACID.

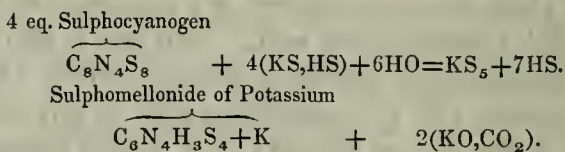
Discovered by Zeise. Prepared by saturating 1 volume of absolute alcohol at the temperature of 50° with ammoniacal gas, and adding to the solution a mixture of 0.16 vol. of bisulphuret of carbon, and 0.4 vol. of alcohol ; the whole should be placed in a well-stopped glass vessel, which is kept perfectly full at the temperature of 60° . Two products are thus produced, of which the one is a compound of ammonia with an acid formed of sulphuret of carbon and sulphuretted hydrogen ; this ammoniacal salt separates in the course of some hours as a crystalline deposit, and the residual liquid contains another ammoniacal salt, the acid of which may be considered as a compound of hydro-sulphocyanic acid and hydrosulphuric acid. This salt is also deposited in a crystalline form when the solution is strongly cooled. By decomposing this ammoniacal salt by hydrochloric acid, an oily substance is obtained, which is the acid of the salt ; it is rapidly decomposed by water.

SULPHOMELLONE.

This is a new compound radical, recently discovered by Mr. Jamieson, who has not, however, yet obtained it in a separate form. When the orange-yellow powder, described under sulphocyanogen, is dissolved to saturation in a strong and hot solution of hydrosulphuret of sulphuret of potassium, KS, HS , and the solution acidulated with acetic acid, a precipitate is obtained, which consists of the hydrogen acid of the new radical, and a little sulphur. It is dissolved in weak ammonia which leaves the sulphur, and the solution, after being decolorized by animal charcoal, gives, on the addition of a mineral acid, a white precipitate of the new acid *hydrosulphomellonic acid*. It is very sparingly soluble in water, but the solution in hot water deposits it in crystals. It is also insoluble in alcohol and ether. When heated it gives off sulphuretted hydrogen, leaving a residue of mellone. Boiled with strong acids, it yields sulphuretted hydrogen and cyanuric acid. It combines readily with bases, forming salts which crystallize with great facility.

Its composition is $C_6N_4H_4O_4$, and it therefore contains the elements of 1 eq. mellone and 4 eq. sulphuretted hydrogen. In the above formula, 1 eq. hydrogen is replaceable by metals, so that, viewed as a hydrogen acid, the hydrosulphomellonic acid is $C_6N_4H_3S_4 + H$; and the hypothetical radical sulphomellone will be $C_6N_4H_3S_4$. The salts formed by this acid with alkaline and earthy bases may be obtained by dissolving the acid in caustic potash or soda, and by boiling the acid with the carbonates of lime, baryta, strontia, and magnesia. Sulphomellonide of silver is got by adding nitrate of silver to sulphomellonide of ammonium, and is insoluble and anhydrous. All the others above named are soluble and crystallize beautifully, with 3 eq. water of crystallization in the salts of potassium and sodium, and 2, 5, 4, and 6 eq. in those of calcium, barium, strontium, and magnesium. The general formula for the anhydrous salts is $C_6N_4H_3S_4 + M$.

The production of this acid is easily explained. The orange powder, from which it is formed, contains sulphocyanogen, C_2NS_2 , and when 4 eq. of this body, with 4 eq. of KS, HS , and 6 eq. water act on each other, there are formed pentasulphuret of potassium KS_5 , sulphuretted hydrogen, sulphomellonide of potassium, and carbonate of potash.



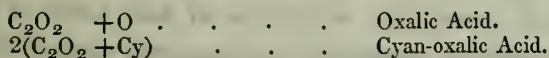
When sulphomellonide of potassium is decomposed by an acid, hydrosulphomellonic acid is formed, just as hydrocyanic and hydromellonic acids are formed from cyanide and mellonide of potassium. With hydrochloric acid, for example, $C_6N_4H_3S_4, K + HCl = KCl + C_6N_4H_3S_4 + H$.

The above description of these very interesting compounds is abridged from Mr. Jamieson's paper in the *Annalen der Chemie und Pharmacie* for September 1846, to which the reader is referred for details. The existence of these compounds is of considerable importance to the theory of compound radicals; for certainly the assumption of the radical sulphomellone simplifies the whole study of these new substances in a remarkable manner. There is some reason, also, to suppose that the radical is capable of existing in the separate state. For when the sulphomellonide of potassium is decomposed in solution by a current of chlorine, there is formed a white precipitate which seems to be sulphomellone; but has not yet been fully examined. The characters of the acid and its salts are well defined and entirely analogous to those of acknowledged hydrogen acids and their salts.

HYPOTHETICAL COMPOUNDS OF CYANOGEN AND CARBONIC OXIDE.

Under these compounds the uric acid and the products of its decomposition are described. These substances are distinctly separated from all known bodies by their chemical relations; an explanation of their formation can only be developed by making certain hypotheses, of which the assumption that they contain cyanogen and carbonic oxide is a deduction drawn from their analyses. The compounds belonging to this group are urile, uric acid, alloxan, alloxantine, dialuric, hydurilic, theonuric, and alloxanosulphurous acids, and uramile

The urile, or urilic acid, which may from its composition be also called the cyan-oxalic acid, is an hypothetical compound of nitrogen, carbon, and oxygen, according to the formula $C_8N_2O_4$; it may be considered as a compound of cyanogen and carbonic oxide $2Cy + 4CO$, or as oxalic acid, in which the oxygen which unites with the radical, carbonic oxide, has been replaced by its eq. of cyanogen.



If this acid be represented by the symbol Ul, the compounds are represented by the formulæ —

Rational Formulæ.	Names.	Empirical Formulæ.
Ul + 1 eq. Urea .	= Uric Acid . . .	= $C_{10}N_4H_4O_6$
Ul + O + 5HO .	= Alloxantine . . .	= $C_8N_2H_5O_{10}$
Ul + O_2 + 4HO .	= Alloxan . . .	= $C_8N_2H_4O_{10}$
Ul + 4HO .	= Dialuric Acid . . .	= $C_8N_2H_4O_8$
Ul + 10HO .	= 2 eq. Hydurilic Acid .	= $2(C_8N_2H_5O_{11})$
Ul + $NO_5 + O_3 + 2HO$.	= Nitrohydurilic Acid .	= $C_8N_3H_2O_{14}$
Ul + $NH_3 + 2HO$.	= Uramile . . .	= $C_8N_3H_5O_6$
Ul + $O_2 + 4HO + \left. \begin{array}{l} NH_3 + 2SO_2 \end{array} \right\}$.	= Thionuric Acid . . .	= $C_8N_3H_7O_{14}S_2$
Ul + $O_2 + 4HO + 2SO_2$.	= Alloxanosulphurous Acid .	= $C_8N_2H_4O_{14}S_2$

URIC ACID.

Discovered by Scheele; first pointed out as existing in the excrement of snakes by Vauquelin, in the excrement of silkworms by Brugnatelli, and in cantharides by Robiquet. Is a product of secretion of all carnivorous animals, of birds, and of many insects; is deposited from human urine generally in combination with ammonia, as it cools, as a yellow or brownish powder; the stone-like concretions in the joints of persons labouring under gout contain uric acid in combination with soda or ammonia; it is the basis of most calcareous deposits in the human bladder. The semi-fluid urine of serpents and birds is principally composed of urate of ammonia. The guano (the decomposed excrement of aquatic birds, which covers the surface of many of the smaller

islands of the South Sea, and is used as manure) is also composed in great part of urate of ammonia.

Prep.—The purest and whitest fragments of the chalk-like excrement or urine of serpents are to be dissolved in 30 or 40 parts of boiling water, by the addition of a slight excess of caustic potash, and the solution, after being boiled till the ammonia is expelled, is filtered to separate impurities. With the above amount of water the filtration is rapid, but with less the filter is apt to be choked up by the crystallization of the urate of potash. The clear liquid is heated and an excess of hydrochloric acid added, which separates the uric acid, at first as a bulky translucent mass, which soon contracts into a heavy crystalline powder. This is well washed and dried, and is then pure hydrated uric acid.

In preparing this acid from highly-coloured urate of ammonia, such as that of calculi, of guano, or of the excrement of birds, such as pigeons, eagles, or sea-fowl, the solution in potash, reduced to the bulk of 20 parts of water for 1 of urate, is to be exposed to a current of carbonic acid gas, which causes the separation of acid urate of potash, in the shape of a crystalline mass, which, when well washed with cold water, is snow-white, or at least may be rendered so by a repetition of the operation, if necessary. The pure salt, being dissolved in hot water, is decomposed as above.

By adding hydrochloric acid to a cold saturated solution of neutral urate of potash, the uric acid is obtained in larger crystals, which differ from the crystalline powder above mentioned, in containing 4 eq. of water of crystallization, which are expelled by a heat of 212° .

Prop.—Crystallizes in fine scales of a brilliant white colour and silky lustre, is tasteless and inodorous, heavier than water, almost insoluble in cold, slightly soluble in boiling water; the solution reddens feebly the vegetable colours. It is dissolved by concentrated sulphuric acid, from which it is precipitated by water; in strong hydrochloric acid it is somewhat more soluble than in pure water. Exposed to the destructive distillation, the products of the decomposition of urea are obtained, namely, urea, cyanuric acid, and cyamelide (the insoluble cyanuric acid); also, hydrocyanic acid, a little carbonate of ammonia, and, as a residue, a brown carbonaceous substance which is rich in nitrogen. In this decomposition the hydrated cyanic acid in combination with ammonia is deposited in the neck of the retort as urea. Dissolves in dilute nitric acid with the evolution of equal volumes of pure carbonic acid and nitrogen; the solution contains alloxan, alloxantine, parabanic acid, and ammonia; evaporated and treated with ammonia in excess, it acquires a purple-red colour, a test by which uric

acid may be recognized. Fused with hydrate of potassa, carbonic acid, and cyanate of potassa, and cyanide of potassium are obtained; boiled with peroxide of lead in water, it is decomposed into allantoinic and oxalic acid, and urea is separated. Is insoluble in ether and alcohol. With sulphuric acid it forms a crystalline compound. (Fritzsche.)

Its empirical formula is $C_{10}N_4H_4O_6$, or $2U + (C_2H_4N_2O_2)$.

The latter formula represents uric acid as a compound of urile or cyanoxalic acid with urea; and there is every reason to believe that it contains urea ready formed. In addition to the evidence arising from the action of heat upon it, as well as from the products of its oxidation by peroxide of lead, as above described, Gregory has shewn that when uric acid is acted on by permanganate of potash, urea is found among the products. As urea is never *formed* by oxidation, and moreover, according to Gregory, resists the oxidizing agency of the permanganate, we can hardly avoid the conclusion that urea exists as such in uric acid. This would render the existence of the supposed radical urile or cyanoxalic acid, $C_8N_2O_4$, or $2(C_2O_2 + Cy)$, almost a matter of certainty.

The above formula is supposed by Liebig and Wöhler to represent uric acid as a monobasic acid, $C_{10}N_4H_3O_5.HO$. But the recent researches of Bensch on this acid seem to shew that it is either $C_5N_2HO_2.HO$, or $C_{10}N_4H_2O_4.2HO$. Bensch considers the acid to be monobasic, adopting the halved formula; but as, according to his researches, it has a very marked tendency to form acid salts and double salts, which is the character of a bibasic acid, it is not easy to see why he has not adopted the formula $C_{10}N_4H_2O_4.2HO$, and viewed the acid as bibasic. This view seems to agree with his results better than that which he prefers.

URIC ACID AND THE METALLIC OXIDES.

Uric acid, as above stated, has a great tendency to form acid salts. Bensch has described the neutral and acid urates of potash and soda, but the urates of ammonia, lime, baryta, strontia, and magnesia are only as yet known as acid salts. Now since acid salts of these bases, except ammonia, only occur in the case of polybasic acids, we prefer to consider uric acid as bibasic. The general formula for the neutral urates is, according to Bensch, $C_5N_2HO_2.MO$, or, on the bibasic hypothesis, $C_{10}N_4H_2O_4.2MO$. That for the acid salts is $C_5N_2HO_2.MO + C_5N_2HO_2.HO$ (Bensch), or, on the other view, $C_{10}N_4H_2O_4 \cdot \begin{Bmatrix} MO \\ HO \end{Bmatrix}$. All the urates are very sparingly soluble, but the neutral salts are rather

more soluble than the acid salts. The neutral urates of potash and soda require respectively 40 and 80 parts of boiling water; the acid urates of potash, soda, and ammonia require respectively 80, 120, and 240 parts of the same solvent, for solution. All of them are far less soluble in cold water. The neutral urates are very unstable, being decomposed and converted into acid salts by washing with water, and even by the carbonic acid of the air.

Acid urate of soda constitutes the chalk stones deposited in gouty subjects. The acid urate of ammonia is the chief constituent of the excrement or urine of serpents, birds, and insects.

All the urates are decomposed by the mineral acids, the uric acid being separated.

ALLANTOINE.

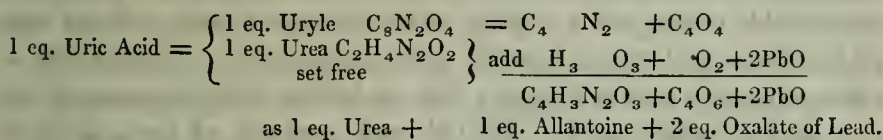
Hist.—Frequently called allantoic acid. Occurs ready formed in the allantoic fluid of the cow (Vauquelin and Buniva); it is formed when uric acid is boiled in water with peroxide of lead. (Wöhler and Liebig.)

Prep.—One part of uric acid is boiled in 20 parts of water, and recently prepared and well-washed peroxide of lead is added in successive portions to the boiling liquid as long as its colour is observed to change. The hot liquid should be filtered, and evaporated until crystals are observed to form upon its surface. The crystals which have deposited when the solution has become quite cold, are purified by recrystallization. Or the allantoic fluid of the cow may be evaporated to one-quarter its volume, and the crystals formed on cooling and long standing are purified by animal charcoal.

Prop.—Small transparent and colourless prisms of the right rhombic system, which have a glassy lustre, are tasteless, have no action on vegetable colours, and are soluble in 160 parts of cold, but more freely in hot water. It is soluble in nitric acid, and is decomposed by it when the solution is boiled, without the evolution of nitrous fumes. Its composition is such, that it contains the elements of anhydrous oxalate of ammonia minus 3 eq. water; this explains its decomposition by the alkalis, by which it is reduced at the boiling heat into an oxalate and ammonia. Gently heated in concentrated sulphuric acid, it is decomposed into carbonic oxide, carbonic acid, and ammonia; but if a strong heat be rapidly applied, the acid is blackened. It is soluble in caustic and carbonated alkalis by the aid of a gentle heat, and may be again obtained unchanged by crystallization. A solution of allantoine in hot water, to which a little ammonia has been added, produces, with the nitrate of silver, a white precipitate, which contains 43.56 per cent. of

oxide of silver, and is composed as represented by the formula $C_8N_4H_5O_5 + AgO$; it consequently contains 2 eq. allantoin, $C_8N_4H_6O_6$ — 1 eq. water, HO + 1 eq. oxide of silver.

In the decomposition of uric acid by the peroxide of lead, 2 eq. of oxygen derived from 2 eq. of the peroxide, and 3 eq. water attach themselves to the constituents of the cyanoxalic acid, by which the latter is decomposed into 2 eq. oxalic acid and 1 eq. allantoin, and the urea is set free.



Its formula is $C_4H_3N_2O_3$, or $2Cy + 3HO$.

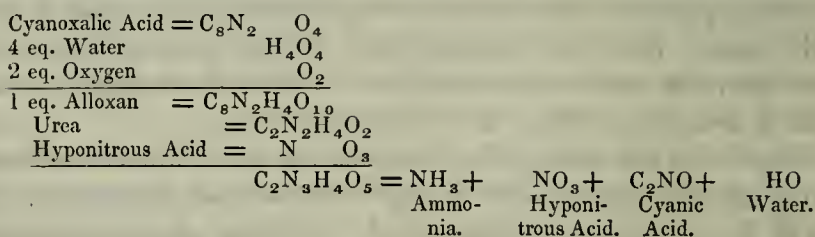
ALLOXAN.

The erythric acid of Brugnatelli; re-discovered by Wöhler and Liebig. One of the products of the decomposition of uric acid by nitric acid. It is best prepared, according to Gregory, by the following method, which is a modification of the original process of Wöhler and Liebig:—Uric acid is gradually added to nitric acid, sp. gr. 1.45, by which it is dissolved with effervescence. The action must be gentle, and, if heat be applied, it must be done cautiously. So much uric acid is added, that the liquid, even while warm, becomes thick with crystals of alloxan, which separate, and which are easily distinguished from undecomposed uric acid. In this way the nitric acid will decompose from $\frac{1}{3}$ to $\frac{1}{2}$ its weight of uric acid. The mass, when cold, is thrown on a funnel, stopped with a little asbestos, and, when it has ceased to drop, the acid liquor remaining in the crystals is carefully displaced by a little ice-cold water. The crystals are purified by solution in water, avoiding a strong heat, and recrystallization. The mother-liquid finally left is not lost, but yields a large quantity of alloxantine, parabanic acid, oxalurate of ammonia, or murexide, if properly treated. (See those compounds.) By this process Gregory obtains, from 100 parts of uric acid, 65 to 75 parts of anhydrous alloxan, equal to from 90 to 105 of the hydrated crystals.

Prop.—On the cooling of a warm but not perfectly saturated solution of alloxan, it is obtained in large colourless and transparent crystals of the right prismatic system, and of a strong adamantine lustre; these crystals effloresce rapidly, losing 25 per cent. — 6 eq. water, and are converted when gently warmed, with the loss of water, into anhydrous alloxan. Gregory states that there are two different kinds of

hydrated crystals: one kind is large, thick, and transparent, of glassy lustre, and does not effloresce so readily; the other is formed of layers of pearly scales, often forming very large masses and efflorescing with very great facility. The latter probably contain more water, but this has not been determined. If a hot saturated solution be allowed to crystallize in a warm place, anhydrous alloxan is deposited directly from the solution in oblique prisms, on the extremities of which truncated rhomboidal octohedrons are seen. It is very soluble in water, has a disagreeable odour, and a slightly saline astringent taste, reddens vegetable colours, and causes a purple stain on the skin. Treated with alkalis, alloxanic acid is formed; but on boiling it is decomposed into urea and mesoxalic acid. Heated with peroxide of lead, it is decomposed into urea and carbonate of lead, with which a few traces of oxalate of lead are mixed. When brought into contact with zinc and hydrochloric acid, or with sulphuretted hydrogen, alloxantine is produced; it is decomposed by free ammonia into mykomelinic acid, by nitric acid into parabanic acid, by sulphuric and hydrochloric acids into alloxantine, by sulphurous acid and ammonia into thionurate of ammonia, with alloxantine and ammonia into murexide. With a protosalt of iron and an alkali, it forms an indigo-blue solution. Does not unite without decomposition with the metallic oxides.

The formation of alloxan, and the other products which arise at the same time, is dependent upon two perfectly independent decompositions; namely, upon the conversion of cyanoxalic acid into alloxan, and upon the mutual decomposition of urea and hyponitrous acid. To 1 eq. of cyanoxalic acid are added the elements of 4 eq. water, and 2 eq. oxygen from 1 eq. nitric acid, by which 1 eq. alloxan and 1 eq. hyponitrous acid are formed. The latter combines with the ammonia of the urea, and liberates cyanic acid; the hyponitrite of ammonia is decomposed by heat into nitrogen and water, and the cyanic acid with water is resolved into carbonic acid and ammonia, which unites with the free nitric acid.



The hyponitrite of ammonia $\text{NH}_3\text{NO}_3 = \text{N}_2 + 4\text{HO}$, and the cyanic acid C_2NO , with 3 eq. water 2HO , yields 2 eq. carbonic acid 2CO_2 , and 1 eq. ammonia NH_3 . If to the products above mentioned

we add alloxantine and parabanic acid, which may be formed by the action of nitric acid on alloxan, the results of this complicated reaction are all clearly accounted for. They are alloxan, alloxantine, parabanic acid, nitrate of ammonia, carbonic acid, and nitrogen. Under certain circumstances nitrate of urea is also formed.

It frequently happens, that, on dissolving the impure alloxan for the purpose of purifying by a second crystallization, a portion of alloxantine is obtained; it may be easily separated from the alloxan by cold water. (See ALLOXANTINE.)

Alloxanic Acid.—Discovered by Wöhler and Liebig. Produced by the decomposition of alloxan by alkalies. It is prepared by decomposing alloxanate of baryta by sulphuric acid. A strongly acid fluid is obtained, which by gentle evaporation crystallizes in radiated groups of acicular crystals; it is a bibasic acid, dissolves zinc, with the evolution of hydrogen, is unchanged by sulphuretted hydrogen, and precipitates the salts of silver, baryta, and lime. The anhydrous alloxanic acid contains the constituents of alloxan minus 2 eq. water; and the hydrated acid has the same composition as anhydrous alloxan.

Its formula is $C_8N_2H_2O_8 + 2HO$.

ALLOXANIC ACID AND METALLIC OXIDES.

Alloxanic acid is a bibasic acid, neutralizes the alkalies perfectly, decomposes the carbonates, and forms, when neutralized by ammonia, with the salts of silver, a white precipitate, which, by boiling, becomes first yellow and then black, the change being accompanied by a rapid effervescence; treated with ammonia in excess, it produces white gelatinous precipitates with the salts of lime, strontia, and baryta; but the precipitate is redissolved by a large excess of water, and readily by an acid. The solutions of the neutral alloxanate of lime, strontia, and baryta become turbid when boiled, the bases are precipitated, and urea and mesoxalic acid are formed.

Alloxanate of Potash: a, *neutral.*—This salt, according to Schlieper, is formed when a strong solution of alloxan is mixed with its own volume of a strong solution of caustic potash, and alcohol added to the mixture till a permanent precipitate begins to appear. On standing 48 hours, the neutral salt is deposited in pure hard transparent crystals. These crystals are $C_8N_2H_2O_8 \cdot 2KO + 6HO$. When heated to 212° , they lose 5 eq. of water. The sixth eq. of water is with difficulty expelled by a heat of 300° .

b, *acid.*—This salt is prepared in the same way, only with an excess of alloxan, 3 or 4 vol. of the solution to 1 vol. of that of potash. It

is thrown down by an excess of alcohol as a crystalline powder, rather sparingly soluble in water, but more soluble in alcohol than the neutral salt. Its solution in water when evaporated yields a gummy mass, which, after long standing, passes into the crystalline modification. This salt has a great tendency to assume the amorphous state.

Its formula is $C_8N_2H_2O_8 + \left\{ \begin{matrix} KO \\ HO \end{matrix} \right\}$.

Alloxanate of Soda possesses this tendency to assume the amorphous state in a still higher degree than the salt of potash, and the gummy mass which it forms is exceedingly deliquescent, so that although it has been seen in crystals, they could only be obtained by long exposure in vacuo to the drying action of sulphuric acid, and then could not be separated from the mother-liquid.

Alloxanate of Ammonia.—The neutral salt resembles that of potash, but is very prone to lose ammonia and pass into the acid salt. The acid salt can only be obtained by adding a slight excess of ammonia to alloxanic acid, and leaving the mixture in a warm place, when the salt forms large transparent crystals; the formula of which is $C_8N_2H_2O_8, \left\{ \begin{matrix} NH_4O \\ HO \end{matrix} \right\}$.

Alloxanate of Baryta: a, neutral.—Prepared by adding barytic water to an aqueous solution of alloxan at the temperature of 140° ; on each addition a white precipitate is formed, but it is redissolved by stirring; the barytic water is added in successive portions till the precipitate is permanent, when the solution is allowed to cool. The mother-liquor separated from the crystals is again to be heated and treated with barytic water as before, and this should be repeated as long as crystals are obtained.

Short transparent needles, or mother-of-pearl scales, which at 212° become milk-white and lose 3 eq. water; at 300° they are anhydrous; they are sparingly soluble in cold, but more freely in hot water; exposed to a red heat they leave a mixture of carbonate of baryta and cyanide of barium. Its formula is $C_8N_2H_2O_8, 2BaO + 4aq$.

b, *acid*.—This salt is best formed by adding chloride of barium to acid alloxanate of ammonia, when on standing the new salt is deposited as a crystalline powder.

Its formula is $C_8N_2H_2O_8 \left\{ \begin{matrix} BaO \\ HO \end{matrix} \right\} + 2aq$.

Alloxanate of Silver.—A white insoluble powder, which produces a slight explosion when heated; the residue after being heated to redness yields cyanic acid and metallic silver.

Its formula is $C_8N_2H_2O_8 + 2AgO$.

Schlieper has described several other salts of alloxanic acid, but the above will be sufficient to give an idea of their general constitution. Some basic alloxanates have been described, but are not much known.

ACTION OF HEAT ON ALLOXANIC ACID.

According to Schlieper, when a strong solution of alloxanic acid is rapidly evaporated in a platinum capsule at a certain temperature, the syrupy residuc begins to give off carbonic acid and to froth up; but at last it flows like oil, and if water be now added, only part of the mass is dissolved, while a sparingly soluble white crystalline powder separates, which is *leucoturic acid*. This substance is so permanent, that it is not affected by boiling with nitric acid of 1.4. It dissolves in alkalies, but with potash it is decomposed, yielding ammonia and oxalic acid; while with ammonia it yields a crystallizable salt. Its formula is $C_6N_2H_3O_6 = C_6N_2H_2O_5 + HO$. This explains the action of potash; for with 3 eq. of water it is resolved into 2 eq. of ammonia and 3 eq. of oxalic acid: $C_6N_2H_3O_6 + 3HO = 2NH_3 + 3C_2O_3$. Leucoturic acid contains the elements of 2 eq. cyanogen, 1 eq. oxalic acid, and 3 eq. water: $2C_2N + C_2O_3 + 3HO = C_6N_2H_3O_6$.

Difluan.—This compound is found in the liquid which has deposited the leucoturic acid. The liquid is evaporated to a syrup and mixed with absolute alcohol, when the new body is precipitated in white flocculent masses. It is washed with alcohol and ether, and dried in vacuo, when it forms a light, bulky, white powder, which is singularly deliquescent. It is very soluble in water, and does not crystallize, neither has it acid properties. Both this and the preceding compounds are readily decomposed by the presence of sulphuric acid in their solutions.

The formula of difluan is $C_6N_2H_4O_5$. This explains the formation of both substances from alloxanic acid, for

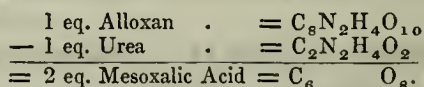
1 eq. Leucoturic Acid	C_6	N_2	H_3	O_6
1 eq. Difluan	C_6	N_2	H_4	O_5
4 eq. Carbonic Acid	C_4			O_8
1 eq. Water			H	O
are equal to 2 eq. Alloxanic Acid.	C_{16}	N_4	H_{10}	O_{20}

The liquid which has deposited the difluan frequently yields on evaporation crystalline crusts of a third body, not named, the formula of which appears to be $C_6N_2H_5O_4$. If this be really so, the three new products have an interesting relation to each other; for on comparing the formulæ, it will be seen, that, as the hydrogen increases, the oxygen diminishes.

Leucoturic Acid	C_6	N_2	H_3	O_6
Difluan	C_6	N_2	H_4	O_5
The third product	C_6	N_2	H_5	O_4

MESOXALIC ACID.

When a saturated solution of alloxanate of baryta or strontia is heated to the boiling point, a precipitate falls consisting of the carbonate, mesoxalate, and alloxanate of baryta or strontia. The solution, on evaporation, yields a crystalline crust, from which urea is separated by treating it with alcohol, and mesoxalate of baryta remains. If a solution of alloxan be added, drop by drop, to a boiling solution of acetate of lead, a very heavy granular precipitate of mesoxalate of lead is formed, and urea remains as the only other product in the solution. The mesoxalic acid may be obtained by decomposing this lead salt by sulphuric acid; it is a strongly acid solution, reddens vegetable colours, and forms, like the alloxanic acid, on the addition of ammonia, precipitates with the salts of baryta and lime, which are soluble in acids and a large excess of water; it may be boiled and evaporated without change. Its action on the salts of silver is characteristic; it forms with them, after being neutralized by ammonia, a yellow precipitate, which on being gently heated is reduced to the metal with a rapid effervescence. The above-mentioned lead salt yields, on analysis, 80.4 per cent. of oxide of lead; it contains a slight admixture of a substance containing nitrogen, probably cyanate or cyanuret of lead, from which it cannot be perfectly purified. The composition of the lead salt is very probably expressed by the formula $C_3O_4 + 2PbO$, in which case its formation from alloxan and alloxanic acid admits of a ready explanation. From 1 eq. alloxan 1 eq. urea is separated, by which 2 eq. of anhydrous mesoxalic acid is left.



The above-mentioned mesoxalate of baryta contains 56 per cent. of baryta, from which its constitution is probably represented by the formula $C_3O_4 + \left\{ \begin{smallmatrix} BaO \\ HO \end{smallmatrix} \right\}$. Mesoxalic acid is therefore most probably a bibasic acid, and is very remarkable as a new compound of carbon and oxygen.

MYKOMELINIC ACID.

Discovered by Wöhler and Liebig. Product of the decomposition of alloxan by ammonia. It is prepared by heating to 212° a solution of alloxan with an excess of ammonia, then neutralizing with an excess of dilute sulphuric acid, and boiling for a few minutes. The mykome-

linic acid falls as a yellow gelatinous precipitate, which dries to a yellow porous powder; it is with difficulty dissolved by cold, but more readily by hot water; the solution has a distinctly acid reaction; it decomposes the carbonated alkalies, and is easily dissolved by the caustic alkalies, but on being boiled with them is decomposed with the evolution of ammonia; it forms with the oxide of silver a yellow compound, which is insoluble in water. It is produced by the decomposition of 1 eq. alloxan and 2 eq. ammonia into 1 eq. mykomelinic acid and 5 eq. water.

Its formula is probably $C_8N_4H_5O_5$.

PARABANIC ACID.

Discovered by Wöhler and Liebig. Product of the decomposition of uric acid and alloxan by nitric acid. Prepared by treating 1 part of uric acid, or 1 part of alloxan, in 8 parts of pretty strong nitric acid, evaporating to the consistence of a syrup, and allowing it to stand for some time, when it yields colourless crystals which may be purified by a second crystallization. It may be obtained in abundance from the mother-liquor of the preparation of alloxan by Gregory's process, if that liquid be gently heated with an additional quantity of nitric acid.

Prop.—Colourless, transparent, thin, hexagonal prisms; has a strong acid taste, very similar to that of oxalic acid; is very soluble in water, does not effloresce either in the air or in a warm room; fuses if heated, when a portion sublimes unchanged, but another part decomposes with the evolution of hydrocyanic acid. The cold solution neutralized by ammonia produces a white precipitate in the salts of silver, which contains 70.62 per cent. of the oxide; when heated with ammonia it is converted into oxaluric acid.

It is formed by the decomposition of 1 eq. of uric acid, which by the addition of 2 eq. of water and 4 eq. oxygen from the nitric acid, is resolved into 2 eq. carbonic acid, 1 eq. parabanic acid, and 1 eq. urea; the latter is decomposed as before mentioned by the hyponitrous acid. One eq. alloxan with 2 eq. oxygen is solved into 2 eq. carbonic acid, 4 eq. water, and 1 eq. parabanic acid.

The formula of the crystalline acid is $C_6N_2O_4 + 2 \text{ aq.}$ It is probably a bibasic acid.

OXALURIC ACID.

Discovered by Wöhler and Liebig. Produced by a metamorphosis of parabanic acid. Prepared by adding dilute sulphuric or hydrochloric acid to a saturated solution of oxalurate of ammonia in hot water, and

rapidly cooling the mixture, when the oxaluric acid falls as a white crystalline powder; this should be washed with cold water till the washing, when neutralized by ammonia, causes with the salts of lime a precipitate which is perfectly redissolved by heat, or by an additional quantity of water. It is a white, or slightly yellow crystalline powder of an acid taste, reddens the vegetable colours, and when neutralized by ammonia, forms with silver salts a white precipitate which is perfectly redissolved by boiling. By boiling in water it is completely decomposed into free oxalic acid and oxalate of urea. The oxaluric acid is formed by the addition of 2 eq. water to the constituents of the parabanic acid. It contains the elements of 2 equivalents of oxalic acid and 1 eq. urea; and it may be considered as uric acid in which the cyanoxalic acid has been replaced by the oxalic acid.

Its formula is $C_6N_2H_3O_7 + aq.$

Oxalurate of Ammonia.—This salt may be formed by heating a solution of parabanic acid with ammonia, or more advantageously by treating a recently prepared solution of uric acid in dilute nitric acid with an excess of ammonia and evaporating. The liquid acquires at first a purple colour, which disappears during the evaporation, and if allowed to cool when arrived at a certain degree of concentration, it deposits radiated groups of hard acicular yellow crystals; they are obtained colourless by charcoal and recrystallization.

The oxalurate of ammonia crystallizes in radiated groups of fine acicular crystals, which have a silky lustre, and are readily dissolved by hot, but with difficulty by cold water; the solution has no reaction on vegetable colours, and may be boiled and evaporated without change; the dry salt loses no weight at 250° , but at a higher temperature it is decomposed with the rapid evolution of hydrocyanic acid, ammonia, and oxamide. (Gregory.) Acids separate from a concentrated solution the oxaluric acid as a crystalline powder.

Its formula is $NH_4O + C_6N_2H_3O_7.$

OXALURIC ACID AND METALLIC OXIDES.

The oxaluric acid forms with the alkalies very soluble, but with the alkaline earths sparingly soluble salts. If concentrated solutions of oxalurate of ammonia and chloride of calcium or barium, be mixed with each other, after standing some time, brilliant transparent scales or needles of oxalurate of baryta or lime will be deposited; a solution of the latter in water, when treated with an excess of ammonia, gives a basic salt in the form of a transparent gelatinous precipitate, which is redissolved by a large quantity of water.

Oxalurate of Silver.—This salt is obtained by mixing boiling solutions of oxalurate of ammonia and nitrate of silver, and is deposited as the solution cools in long anhydrous needles of a silky lustre; these are decomposed at a high temperature without explosion.

Its formula is $\text{AgO} + \text{C}_6\text{N}_2\text{H}_3\text{O}_7$.

ALLOXANOSULPHUROUS ACID.

This acid is formed, according to Gregory, when sulphurous acid is added in excess to a solution of alloxan, and the mixture is neutralized by potash. In a short time, beautiful transparent hard crystals are deposited, which contain the new acid united with potash. The acid appears to contain 1 eq. alloxan and 2 eq. sulphurous acid, but has not yet been isolated.

THIONURIC ACID.

A bibasic acid. Discovered by Wöhler and Liebig. Is formed by the action of sulphite of ammonia on alloxan. It is prepared by decomposing the thionurate of lead by hydrosulphuric acid. A white crystalline mass, is permanent in the air, and readily dissolved by water; of an acid taste, reddens vegetable blues strongly; its saturated solution, when heated to the boiling point, congeals to a semifluid crystalline mass of uramile, and the fluid when this has deposited is found to contain free sulphuric acid. The thionuric acid contains the elements of 1 eq. alloxan, 1 eq. ammonia, and 2 eq. sulphurous acid; the uramile may be considered as a compound of ammonia with alloxan minus 2 eq. oxygen, or of cyanoxalic acid with 1 eq. ammonia and 2 eq. water. On heating the solution of thionuric acid 2 eq. oxygen are given by 1 eq. alloxan to the 2 eq. of sulphurous acid, which is thus converted into sulphuric acid, while the elements of cyanoxalic acid, ammonia, and water combine to form uramile.

Its formula is $\text{C}_8\text{N}_3\text{H}_7\text{O}_{14}\text{S}_2$, or $\text{C}_8\text{N}_2\text{H}_4\text{O}_{10} + \text{NH}_3 + 2\text{SO}_2$, that is, 1 eq. alloxan, 1 eq. ammonia, and 2 eq. sulphurous acid. But as it contains 2 eq. of water, capable of being replaced by bases, the true formula probably is $(\text{C}_8\text{N}_3\text{H}_5\text{O}_8, 2\text{SO}_2) + 2\text{HO}$.

Thionurate of Ammonia.—*Prep.*—A cold solution of alloxan is mixed with an excess of an aqueous solution of sulphite of ammonia; the mixture is then treated with pure ammonia in excess, and boiled for five minutes. As the solution cools, the thionurate of ammonia crystallizes, so as nearly to fill the solution, and may then be washed with a little cold water, and dried.

Prop.—Quadrangular scales of a strong mother-of-pearl lustre, which lose at 212° 6 per cent. = 2 eq. water, and acquire a pink colour;

sparingly soluble in cold, freely in boiling water. If a solution of this salt be heated with a dilute mineral acid, it suffers the same decomposition as the free acid; mixed with nitrate of silver, the metal is after some time deposited of a brilliant metallic lustre. If to a solution of the salt a quantity of hydrochloric acid be added sufficient to neutralize half the ammonia which it contains, and if the solution be then evaporated in a water-bath, a soft white acid thionurate of ammonia in thin acicular crystals is obtained, which when boiled is decomposed into ammonia and uramilic acid.

Formula of thionurate of ammonia, $(C_8N_3H_5O_8, 2SO_2) + 2NH_4O + 2 \text{ aq.}$

THIONURIC ACID AND METALLIC OXIDES.

Thionuric acid forms with the alkalis very soluble salts; with the alkaline earths either insoluble or sparingly soluble salts, which are however readily dissolved by dilute acids; they generally are formed of 1 eq. of acid and 2 eq. of the metallic oxide. All these salts evolve sulphurous acid abundantly when treated with concentrated sulphuric acid; when fused with hydrate of potassa, sulphite of potassa is formed.

Thionurate of Lime.—Prepared by mixing a hot solution of thionurate of ammonia with nitrate of lime. It crystallizes in short fine prisms of a silky lustre.

Thionurate of Baryta.—The barytic salts are precipitated even by very dilute solutions of the thionurates in thick gelatinous flakes, which are readily redissolved by acids.

Thionurate of Lead.—A thick gelatinous precipitate, which rapidly changes in warm water to fine short needles of a white colour; on drying they lose water and become pink. Exposed to the destructive distillation they yield urea, together with a peculiar substance which crystallizes in large broad tables.

Thionurate of Zinc.—Small crystalline concretions of a lemon-yellow colour.

URAMILE.

Discovered by Wöhler and Liebig. A product of the decomposition of thionuric acid.

Prep.—A hot saturated solution of thionurate of ammonia is treated with hydrochloric acid till it has a strongly acid reaction, boiled till a slight turbidity is observed, when the whole is soon converted to a semifluid mass. It is obtained in a plume-form aggregation of fine but hard needles, or as a fine porous powder, consisting of fine needles which have a silky lustre, and are permanent in the air, but acquire a

pink tint when heated ; insoluble in cold, but taken up in small quantity by boiling water ; soluble in ammonia and the caustic alkalies in the cold, from which it is precipitated by acids unchanged. Uramile is formed from thionuric acid ($C_8N_3H_5O_8, 2SO_2$) by the conversion of the 2 eq. sulphurous acid into sulphuric acid ; $C_8N_3H_5O_8, 2SO_2 = C_8N_3H_5O_6 + 2SO_3$. When thionuric acid alone is used, the sulphuric acid is set free. When thionurate of ammonia is boiled with an acid, the ammonia is removed by the acid employed, and the thionuric acid, being set free, undergoes the above decomposition. The solution of uramile in ammonia and caustic potassa acquires a purple colour by exposure to the air, and deposits green acicular crystals of a brilliant metallic lustre ; if boiled in the caustic potassa, it is decomposed into uramilic acid with the evolution of ammonia. It is soluble in concentrated sulphuric acid, from which it is again precipitated by water ; by boiling in dilute acids it suffers the same change as in caustic potassa. By boiling with the oxides of silver and mercury it is converted into murexide, and the oxide is reduced. With concentrated nitric acid it is resolved into alloxan, with the evolution of hyponitrous acid, and the formation of nitrate of ammonia. Uramile may be considered as uric acid, in which the urea is replaced by 1 eq. ammonia and 2 eq. water.

Its formula is $C_8N_3H_5O_6$, or $C_8N_2O_4, NH_3, 2HO$; eq. = 144.41.

URAMILIC ACID.

Discovered by Wöhler and Liebig. A product of the decomposition of uramile.

Prep.—A saturated solution of thionurate of ammonia in cold water is added to a small quantity of sulphuric acid, and the mixture evaporated in a water-bath, when the uramilic acid is slowly deposited in transparent prisms of a glassy lustre. If a white amorphous deposit, which is soluble in hot water, be at the same time obtained, it arises from the presence of undecomposed acid thionurate of ammonia ; this is again dissolved in water mixed with sulphuric acid, and treated as before.

Prop.—Colourless four-sided prisms, or fine silky needles ; is soluble in 6—8 parts of cold, and in 3 parts of boiling water ; loses no weight when heated to 212° , but acquires a slightly pink colour ; the solution has a feeble acid reaction. It is soluble in concentrated sulphuric acid with effervescence, but without colouring the acid. By boiling in strong nitric acid, a yellow solution is obtained, which yields on evaporation white crystalline and sparingly soluble scales or granu-

lar crystals; they are dissolved by alkalis, and again precipitated by acetic acid. In the formation of uramilic acid 2 eq. of uramile lose the elements of 1 eq. of ammonia, which are replaced by 3 eq. of water.

Its formula is $C_{16}N_5H_{10}O_{15}$.

Liebig and Wöhler were not able to reproduce this acid, and Gregory has been equally unsuccessful. The latter suggests that uramilic acid may possibly be the acid dialurate of ammonia.

SALTS OF URAMILIC ACID.

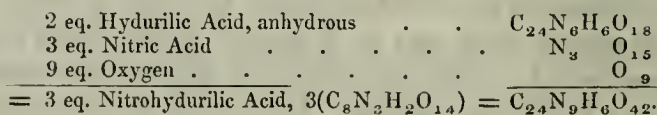
The uramilic acid forms with ammonia and the fixed alkalis soluble crystallizable salts; lime and baryta are not thrown down from their saline solution by the free acid; but on the addition of ammonia a white precipitate is formed, which again disappears in a large quantity of water. Uramilate of ammonia produces with nitrate of silver a dense white precipitate, which contains from 63—64 per cent. of silver. (Liebig and Wöhler.)

HYDURILIC ACID.

Schlieper, on one occasion, while endeavouring to prepare alloxan, with nitric acid of sp. gr. 1.25, obtained, along with the alloxan, a new compound, which he could not afterwards reproduce. This turned out to be the acid ammoniacal salt of a new acid, to which he gave the name of hydurilic acid. It appears, when separated from the ammonia by stronger acids, as a light powder, composed of minute acicular crystals, and appears to be a bibasic acid, $C_{12}N_3H_5O_{11} = C_{12}N_3H_3O_9 + 2HO$. 2 eq. of it contain the elements of 3 eq. urilic acid and 10 eq. water. $3(C_8N_2O_4) + 10HO = 2(C_{12}N_3H_5O_{11})$. Hence the name.

Nitrohydurilic Acid.—The preceding acid, when acted on by nitric acid, yields a new acid, containing in 3 eq. the elements of 2 eq. hydurilic acid, 3 eq. nitric acid, and 9 eq. oxygen.

Its formula is $C_8N_3H_2O_{14}$, and



This acid explodes when heated. Its salts, for want of materials, have not been studied.

ALLOXANTINE.

First observed by Prout as a product of the decomposition of uric acid by nitric acid; it is also formed by the action of chlorine on uric acid, as likewise from alloxan by the action of deoxidizing agents.

Prep.—*From uric acid*: one part of uric acid is added to 32 parts of water, which is brought to the boiling point, and then treated with dilute nitric acid in successive portions till a perfect solution is obtained; it should then be evaporated to two-thirds of its volume, when, after standing for some hours or a day, crystals of alloxantine will be deposited, which should be purified by re-crystallization.—*From alloxan*: it is obtained in large quantity by transmitting a stream of hydrosulphuric acid gas through a solution of alloxan, when first sulphur, and then a crystalline mass of alloxantine is deposited; it is separated from the sulphur by solution in hot water, which yields by evaporation and cooling pure crystals of alloxantine. It may also be formed by adding zinc and hydrochloric acid to a solution of alloxan, but here an excess of acid must be carefully avoided; or by boiling alloxan in moderately strong sulphuric acid, when it is deposited as the solution cools. Diluted hydrochloric acid, and even diluted nitric acid, produce the same effect. The latter fact is curious, because stronger nitric acid reconverts alloxantine into alloxan; and also because the conversion of alloxan into alloxantine is a process of deoxidation. The reaction, in this mode of preparation, however, is different from that which occurs when sulphuretted hydrogen is employed. It is explained below for sulphuric acid, and the explanation applies to nitric and hydrochloric acids. (Gregory.) If a solution of alloxan be exposed to the action of a galvanic battery, oxygen is evolved at the positive electrode, while the negative is covered with a crystalline crust of alloxantine. When a solution of alloxan is boiled, it is converted into alloxantine, parabanic acid, and carbonic acid. $3(\text{C}_8\text{N}_2\text{H}_4\text{O}_{10}) = 2(\text{C}_8\text{N}_2\text{H}_5\text{O}_{10}) + \text{C}_6\text{N}_2\text{H}_2\text{O}_6 + 2\text{CO}_2$. This is the reason why solutions of alloxan should never be heated beyond 120° .

Prop.—Short oblique four-sided prisms of the oblique prismatic system, the obtuse angle of the prism being 105° . The crystals are colourless, or have a slightly yellow tint; in an ammoniacal atmosphere they become red, acquire a greenish metallic lustre, and are readily reduced to powder; exposed to 212° they undergo no change of weight, but at 300° lose 15.4 per cent. = 3 eq. water; sparingly soluble in cold, more freely in boiling water. The solution reddens litmus; is converted into alloxan by being warmed with strong nitric acid, or by a solution of chlorine; forms with the salts of silver a black precipitate

of metallic silver; it is decomposed by alkalies; barytic water causes a violet-blue precipitate, which is first rendered colourless by heat and then disappears; by adding an excess of baryta to this solution a brilliant white precipitate is formed.

By the action of dilute nitric acid upon uric acid, only 1 eq. of oxygen is taken up by the cyanoxalic acid, and there is formed by the addition of the elements of 5 eq. of water, 1 eq. alloxantine and nitrous acid, which is decomposed by the water into $\frac{1}{2}$ eq. of hyponitrous acid, and $\frac{1}{2}$ eq. nitric acid; the former reacts as described in alloxan upon half of the urea liberated, causing their mutual decomposition, while the other half of the urea combines with the nitric acid to nitrate of urea. In its preparation from alloxan 1 eq. oxygen of the latter is converted, by the hydrogen of the sulphuretted hydrogen, into water, which remains in combination with the other elements. On boiling alloxan with sulphuric acid 2 eq. are decomposed into 1 eq. alloxantine, 3 eq. oxalic acid, 1 eq. ammonia, and 1 eq. cyanic acid; the latter being decomposed, together with 3 eq. water, into carbonic acid and ammonia. If a solution of alloxan, instead of being left in contact with zinc and hydrochloric acid at common temperature, be heated to the boiling point, and kept at that temperature for some time, it deposits, on cooling, yellow granular crystals of a brilliant lustre and sparing solubility in boiling water, and of characters essentially different from alloxantine.

Its formula is $C_8N_2H_5O_{10}$, or $C_8N_2O_4 + O + 5HO$; eq. = 162.26.

PRODUCTS OF THE DECOMPOSITION OF ALLOXANTINE.

DIALURIC ACID.

If a stream of sulphuretted hydrogen gas be passed through a boiling solution of alloxantine, a further precipitation of sulphur ensues, and the solution acquires a strongly acid reaction; if neutralized by carbonate of ammonia, it deposits on cooling an abundant crop of white silky acicular crystals of an ammoniacal salt, which, when heated to 212° in the air, becomes of a blood-red colour; its composition is represented by the formula $C_8N_3H_7O_8$, and it may therefore be considered to contain the elements of cyanoxalic acid with 1 eq. ammonia and 4 eq. water. But it is the ammoniacal salt of a new acid, dialuric acid, the formula of which is $C_8N_2H_3O_7, HO$. The dialurate of ammonia was described and analyzed by Liebig and Wöhler, but, for want of material, they did not succeed in isolating the acid. Gregory subsequently did so, and his analysis confirmed the prevision of the

former chemists. According to Gregory, the dialurate of ammonia is best obtained by adding a slight excess of hydrosulphuret of ammonia, along with some carbonate of ammonia, to a solution of alloxan or alloxantine, when a copious crystalline precipitate appears. This, when boiled, dissolves in the liquid, and on cooling is deposited in minute silky prisms, which are white, but in drying become pink or even deep red. They should be washed on the filter, first with diluted hydrosulphuret of ammonia, then with alcohol, to which a little hydrosulphuret has been added; and, lastly, with pure alcohol; and dried by pressure in blotting-paper, and in the vacuum of the air-pump. They may thus be obtained white, or very nearly so; and when once quite dry, they are permanent. When this salt is dissolved in hot and moderately strong hydrochloric acid, crystals of dialuric acid are deposited on cooling. These crystals resemble somewhat those of alloxantine, but are larger, and not so brilliant. Their solution, and the crystals themselves under water, absorb oxygen, and are soon changed into alloxantine, from which dialuric acid only differs by 1 eq. oxygen and 1 eq. water.

Dialuric acid is a powerful acid. Its salts are insoluble or sparingly soluble, and only permanent in the dry state. The dialurate of ammonia, above described, is the most interesting.

Its formula is $C_8N_3H_7O_8 = NH_4O + C_8N_2H_3O_7$.

ALLITURIC ACID.

When a solution of alloxantine is boiled with hydrochloric acid, and the residue acted on by nitric acid, there is formed this new acid, which is insoluble in nitric acid. It is crystallizable, and forms a crystallizable salt with ammonia, but is decomposed by potash.

Its formula is $C_8N_2H_3O_4 = C_8N_2H_2O_3 + HO$.

When boiled with potash, ammonia is expelled, and the solution, on the addition of acids, yields a precipitate which appears to be a compound of potash with an acid composed of $C_{18}N_5H_8O_{18}$; which might be derived from 3 eq. allituristic acid, 2 eq. water, and 4 eq. oxygen, *minus* 1 eq. ammonia.

DILITURIC ACID.

When the liquid which had deposited the allituristic acid was treated with sulphuretted hydrogen to convert into alloxantine any alloxan that might be present, the alloxantine removed, and the residue acted on by nitric acid with a view to obtaining parabanic acid, a yellow sub-

stance separated during evaporation, which proved to be the ammoniacal salt of a new acid, dilituric acid. (Schlieper.) This salt, when purified by solution in hot water, crystallizes in brilliant yellow scales. The acid is remarkable for the energetic affinities which it exhibits, which, in fact, render it impossible at present to isolate it. The salt dissolves in strong sulphuric acid with the aid of heat, and that without losing ammonia or undergoing any change. The diliturate of ammonia is $\text{NH}_4\text{O} + \text{C}_8\text{N}_3\text{H}_2\text{O}_9$; but there is reason to believe that the acid is bibasic, and that the true formula of the above salt is $\text{C}_8\text{N}_3\text{HO}_8 + \left\{ \begin{smallmatrix} \text{NH}_4\text{O} \\ \text{HO} \end{smallmatrix} \right\}$. This salt when heated, is decomposed with a slight explosion, but the diliturates of potash and silver explode like the fulminates. This may arise from the circumstance that the acid contains the elements of 3 eq. cyanic acid, 2 eq. carbonic acid, and 1 eq. water, $3(\text{C}_2\text{NO}) + 2\text{CO}_2 + \text{HO} = \text{C}_8\text{N}_3\text{HO}_8$. The cyanic acid, it will be remembered, is polymeric with the fulminic acid.

If a hot saturated solution of alloxantine be treated with a solution of sal-ammoniac, it instantly acquires a purple-red colour, which disappears after a few moments, while the solution becomes turbid, and deposits brilliant white scales of uramile, which are pink when dried; the same occurs with the acetate, the oxalate, and other ammoniacal salts; the solution contains, after the decomposition, alloxan and free hydrochloric acid. Two eq. alloxantine and 1 eq. ammonia contain the elements of 1 eq. uramile, 1 eq. alloxan, and 4 eq. water. By heating a solution of alloxantine in pure ammonia, the products first formed are uramile and mykomelinate of ammonia, both of which suffer further changes by the continued action of ammonia and the atmospheric air. If a solution of alloxantine in ammonia, which has been prepared in the cold, be spontaneously evaporated by exposure to the air, oxygen is absorbed, and crystals of the oxalurate of ammonia are obtained: 3 eq. alloxantine, 7 eq. oxygen, and 6 eq. ammonia, contain the elements of 4 eq. oxalurate of ammonia and 5 eq. water.

If oxide of silver be heated in a solution of alloxantine, a portion of the former is reduced with effervescence, and the solution contains pure oxalurate of silver. In this reaction 3 eq. oxygen from the oxide of silver decompose 1 eq. alloxantine into 1 eq. water, 2 eq. carbonic acid, and 1 eq. oxaluric acid, which last unites with some undecomposed oxide of silver. Peroxide of mercury is dissolved by alloxantine without effervescence, and the solution appears to contain alloxanate of the protoxide of mercury. A solution of alloxantine by boiling with peroxide of lead is decomposed into urca and carbonate of lead.

MUREXIDE.

The purpurate of ammonia discovered by Prout. *Prep.*—By heating a mixture of equal parts of peroxide of mercury and uramile in 36—40 parts of water, with the addition of an exceedingly small quantity of ammonia; as soon as the liquid has acquired a deep purple colour, it is filtered and allowed to rest, when the murexide crystallizes; or by dissolving uramile by the aid of heat in ammonia, and when the solution has cooled to 160° , alloxan is added until a very slight alkaline reaction is observed. Or a solution of uric acid in dilute nitric acid is evaporated until it acquires a flesh-red colour, when it is allowed to cool to 160° , and is then treated with a dilute aqueous solution of ammonia, till the presence of free ammonia is remarked by the odour; the solution is then diluted with half its volume of boiling water, and allowed to cool. In this method of preparation, it is advisable to test a small quantity of the solution of uric acid from time to time by saturating it with ammonia: if it be rendered turbid by the ammonia, and a red powder falls, a small quantity of nitric acid must be added to the hot solution of the uric acid; but if a yellow slimy precipitate be formed, the solution will only give rise to the formation of murexide after a stream of sulphuretted hydrogen has been transmitted through it. Or a boiling saturated solution of alloxantine in water is treated with ammonia in excess till the precipitated uramile is redissolved, when a solution of alloxan is added, so that only a slight alkaline reaction is left, and the whole is allowed to cool. Or by heating alloxantine with sal-ammoniac or oxalate of ammonia, and after the formation of uramile adding ammonia till the former is redissolved, and then alloxan. Murexide may be formed by a number of other processes, by bringing together many of the products of uric acid with ammonia, with or without the presence of atmospheric air. The easiest and most certain method, which is also the most productive, is the following, proposed by Liebig, and slightly modified by Gregory. Seven grains of hydrated alloxan and 4 grains of alloxantine are dissolved by boiling in 240 grains of water, and the boiling solution added to 80 grains by measure of a cold and strong solution of carbonate of ammonia. This mixture has precisely the proper temperature, and deposits very fine crystals of murexide. The experiment is not so successful on a large scale, probably because the liquid, by remaining longer warm, undergoes a partial change. It is best to try first a saturated solution in cold water of carbonate of ammonia. If it do not yield good crystals, add a little water, and try it again, and so on till a solution of the carbonate is ob-

tained which gives a good result. The difficulty is owing to the spontaneous formation of different carbonates by the action of water on the carbonate of the shops; but when a proper solution is obtained the experiment never fails, and is well adapted for the lecture-table.

When the oxygen from $1\frac{1}{2}$ eq. of peroxide of mercury is added to 2 eq. uramile, they may give rise to the formation of 1 eq. murexide, 1 eq. alloxanic acid, and 3 eq. water. Alloxan appears to have the same action upon a solution of uramile in ammonia as the peroxide of mercury. One eq. alloxan, 2 eq. alloxantine, and 4 eq. ammonia, contain the elements of 2 eq. murexide and 14 eq. water. The solution of uric acid in dilute nitric acid contains principally alloxantine, urea, and nitrate of ammonia: evaporated until the flesh-red colour appears, a portion of the alloxantine is converted by the action of free nitric acid into alloxan, a portion of which, by a further action, gives rise to parabanic acid. But when alloxan and alloxantine are simultaneously present in a solution, an excess of ammonia produces a deep purple-red liquid, from which murexide is deposited. If the solution contain an excess of alloxantine, the crystals of murexide are mixed with uramile; with an excess of alloxan mykonclinate of ammonia is formed, which also falls with the murexide. The parabanic acid present passes, when the solution of uric acid is saturated with ammonia, into oxaluric, which is obtained in crystals of oxalurate of ammonia by evaporating the mother-liquid.

Prop.—Murexide crystallizes in short four-sided prisms, two faces of which, like the upper wings of the cantharides, reflect a green metallic lustre. The crystals are transparent, and by transmitted light are of a garnet-red colour. It forms a brownish-red powder, which, under the polishing steel, acquires a brilliant metallic green colour. It is insoluble in ether and alcohol; sparingly soluble in cold, but more readily in boiling water, on the cooling of which it crystallizes unchanged; insoluble in a saturated solution of carbonate of ammonia, soluble in caustic potassa with a beautiful purple colour, which disappears on the application of heat with the evolution of ammonia. It is decomposed either in the solid state or in solution by all the mineral acids, with the separation of brilliant scales of murexan; the liquid contains ammonia, alloxantine, alloxan, and urea. The instant the murexide is brought into contact with hydrosulphuric acid, it is decomposed into alloxantine, dialuric acid, and murexan, with the separation of sulphur. An equivalent of alloxan, alloxantine, murexan, and urea, together with 2 eq. ammonia, contain the elements of 2 eq. murexide and 11 eq. water.

Its formula is $C_{12}N_5H_6O_8$; eq. = 197.19.

The above formula has been preferred to one or two others, which may also be deduced from the analyses of murexide by Wöhler and Liebig, because, by adopting it, we can explain, in some cases, the formation and the decomposition of murexide. But the composition of murexide cannot be considered as fully ascertained. Indeed, Gregory has suggested that there are most probably two varieties of murexide, agreeing in aspect, but differing in chemical characters and composition. Thus, he found that some specimens do not yield a trace of murexan when acted on by acids, and that murexide sometimes occurs which is very soluble in weak ammonia, while that analysed by Wöhler and Liebig was nearly insoluble, if not quite so, in that liquid. The subject requires careful study, and is of great importance, as the true theory of the formation of murexide must throw light on the formation of those organic colouring matters which are produced, like murexide, by the action of ammonia on colourless substances, such as indigo, litmus, cudbear, &c.

MUREXAN.

The purpuric acid discovered by Prout as the product of the decomposition of murexide. Prepared by dissolving murexide in caustic potassa by the aid of heat, which is applied till the blue colour disappears, when dilute sulphuric acid is added in excess.

Prop.—It falls in crystalline scales of a silky lustre; is insoluble in water and dilute acids, but is taken up by ammonia and the fixed alkalis in the cold without neutralizing them. It is dissolved by concentrated sulphuric acid, from which it is again precipitated unchanged by water. If a solution of murexan in ammonia be exposed to the air, it acquires a purple-red colour, and deposits the brilliant crystals of murexide; with an excess of ammonia the solution again becomes colourless, and is then found to contain oxalurate of ammonia. Two eq. murexan, 1 eq. ammonia, and 3 eq. oxygen, contain the elements of 1 eq. murexide and 3 eq. water; 1 eq. murexan, 3 eq. oxygen, and 1 eq. ammonia are the constituents of 1 eq. oxalurate of ammonia.

Its formula is $C_6N_2H_4O_5$; eq. = 109.02.

The properties of murexan closely resemble those of uramile, and the difference in their composition in 100 parts is not very great. In addition to the properties above mentioned, Gregory states that murexan, if boiled with water, peroxide of mercury, and a little ammonia, yields murexide just as uramile does. It is possible that these two substances may be essentially the same.

APPENDIX TO THE COMPOUNDS OF URIC ACID.

Uric Oxide, or Xanthic Oxide.—A rare constituent of urinary calculi; first discovered by Marcet.

Prep.—Urinary calculi, which contain this ingredient, are dissolved in caustic potassa, and the solution saturated with carbonic acid, when the uric oxide is precipitated.

Prop.—A white precipitate; when dried, it forms a pale yellow hard mass, which acquires a waxy lustre by friction: it is dissolved by the pure and carbonated alkalis; in small quantity by hot water, hydrochloric and oxalic acids. It is soluble in concentrated sulphuric acid with a yellow colour; no precipitation is caused by the addition of water to the solution. It is dissolved in nitric acid without effervescence; on evaporating to dryness, a lemon yellow residue is left, which is not reddened by ammonia, is partially soluble in water, but perfectly and easily in potassa; the solution has a light reddish-yellow colour, and leaves on evaporation a red residue. Exposed to the destructive distillation, it evolves an odour of urine, hydrocyanic acid, and carbonate of ammonia, but no urea. The calculi, which contain uric oxide, have a light brown, or bright brown surface; the fracture is scaly, of a strong lustre, and also of a brown or deep flesh colour; by friction the surface becomes resinous.

Its formula is $C_5N_2H_2O_2$.

Cystic Oxide.—Discovered by Wollaston; a rare constituent of urinary calculi; an organic base.

Prep.—The calculus is dissolved in aqueous ammonia, and the filtered solution evaporated in the air, when the cystic oxide crystallizes.

Prop.—In the calculus it exists as a yellowish-white confused crystalline mass of a brilliant lustre: crystallizes from its solution in potassa, on the addition of acetic acid, in hexagonal plates; from ammonia, in white transparent scales. It is decomposed by heat, with the evolution of sulphurous and ammoniacal products of an offensive odour. It is readily dissolved by mineral acids, with which it forms crystalline compounds. It forms with hydrochloric acid an anhydrous salt, which is composed of 1 eq. of the base and acid. The salt with nitric acid is formed of 1 eq. of acid, 1 eq. of base, and 2 eq. water, the half of which is separated by a temperature of 105° . It is soluble in the pure and carbonated alkalis; but if the solution be heated it is decomposed at first with the evolution of ammonia, but, as the evaporation proceeds, a very combustible gas, which burns with a blue flame, and

smells like sulphuret of carbon, is given off. The occurrence of the cystic oxide is so rare, that it is impossible to institute any investigation of this remarkable substance.

According to the analysis of Thaulow, its formula is $C_6NH_6O_4S_2$.

Guanine.—Discovered by Unger; a product of the spontaneous decomposition of uric acid or urate of ammonia in guano. It is found in all kinds of guano, but especially in Peruvian. It is extracted by hydrochloric acid, which forms soluble compounds with it; and being insoluble in water, it is precipitated by alkalis from the solution.

Guanine appears as a crystalline powder, which, when pure, is white. It is possessed of basic properties; and, forms crystallizable salts with most acids. Its formula is $C_{10}N_5H_5O_2$; and, as it contains the same number of equivalents of carbon as uric acid does, it is probable that we shall find means of producing it directly from that acid.

The salts of guanine, as far as they have hitherto been examined, present some peculiarities. Thus there are four nitrates of guanine, in which the equivalents of the base are to those of the acid as 1 : 1, 1 : 2, 3 : 4, and 3 : 5, the last three being acid salts. Now acid nitrates are of very rare occurrence. All these nitrates contain water of crystallization. Again, guanine forms a neutral hydrochlorate and a bihydrochlorate, the latter also a very rare form of combination. The compound or double salt of hydrochlorate of guanine and bichloride of platinum contains 2 eq. of the latter salt, and, what is still more unusual, water of crystallization, the corresponding salts of organic bases being always anhydrous. It is possible, however, that, if closely examined, some of them may be found, like that of guanine, to contain water, which has not been looked for from the idea that these double salts are always anhydrous. Guanine forms a neutral sulphate, which is decomposed by water into free acid, and hydrated guanine which is deposited. The following table exhibits the composition of the salts of guanine above mentioned.

	Guanine.	Acid.	Water.
Hydrochlorate, Neutral	$C_{10}N_5H_5O_2$	+ HCl	+ 7HO
Ditto, Acid	$C_{10}N_5H_5O_2$	+ 2HCl	
Sulphate	$C_{10}N_5H_5O_2$	+ HO,SO_3	+ 2HO
Nitrate, Neutral	$C_{10}N_5H_5O_2$	+ NO_5	+ 4HO
Ditto, Acid	$C_{10}N_5H_5O_2$	+ $2NO_5$	+ 6HO
Ditto, ditto	$3(C_{10}N_5H_5O_2)$	+ $4NO_5$	+ 12HO
Ditto, ditto	$3(C_{10}N_5H_5O_2)$	+ $5NO_5$	+ 16HO
	Hydrochlorate of Guanine.	Bichloride of Platinum.	Water.
Platinum, Double Salt	$C_{10}N_5H_5O_2.HCl + 2(PtCl_2) + 4HO.$		

Guanine is a weak base, and even enters into combination with bases as if it had also feeble acid properties. Thus it forms with soda

a compound, the formula of which is $C_{10}N_5H_5O_2 + 2NaO + 6HO$, and which is decomposed both by water and by carbonic acid.

Guanine was at first described as uric or xanthic oxide, the occurrence of which in guano was quite conceivable, and very interesting; but more full investigation has established the existence of guanine as a distinct compound, while the uric or xanthic oxide continues as rare as it formerly was. The formula of the latter, if reduced to the same number of eq. of carbon, is $C_{10}N_4H_4O_4$, which is uric acid, $C_{10}N_4H_4O_6$, minus 2 eq. of oxygen. Hence the term uric oxide. Now guanine, $C_{10}N_5H_5O_2$, contains 2 eq. of oxygen less than uric oxide, with 1 eq. of nitrogen and 1 eq. of hydrogen more. It is possible, therefore, that by oxidation both uric oxide and uric acid may be obtained from guanine; and we can also see how, from uric acid, by reduction, uric oxide may be formed, and how from either of those bodies, by the addition of 1 eq. of ammonia and the subtraction of the elements of water, guanine may be formed. For uric acid $C_{10}N_4H_4O_6$, with 1 eq. of ammonia NH_3 , gives $C_{10}N_5H_7O_6$; and if from this sum we remove 2 eq. of water and 2 eq. of oxygen, guanine remains. Or uric oxide $C_{10}N_4H_4O_4$, plus 1 eq. ammonia NH_3 , and minus 2 eq. water $2HO$, gives guanine. It is hardly to be doubted, that, as our means of applying reducing agencies, slow and powerful, like those of the animal body, to uric acid, increase, we shall succeed in obtaining from it either uric oxide or guanine or both of these compounds.

Hyperuric Acid.—This name has been given by Unger to an acid obtained by the oxidation of guanine by means of chlorate of potash and hydrochloric acid. It forms brilliant colourless crystals sparingly soluble in water and acids. The analysis of Unger, which, however, is only to be regarded as an approximation, yielded the formula $C_{10}N_4H_3O_7 + 2HO$ for the acid, and $C_{10}N_4H_3O_7 + 2AgO$ for the silver salt. In this case it is a bibasic acid, and the anhydrous acid may be easily derived from anhydrous uric acid by oxidation. If uric acid be considered as monobasic, with the formula $C_{10}N_4H_3O_5 + HO$, the addition of 2 eq. oxygen to the anhydrous acid, and 1 eq. of basic water, would give hyperuric acid. Hence the name. If, however, uric acid be considered bibasic, $C_{10}N_4H_2O_4 + 2HO$, then, to form hyperuric acid, it is only necessary to add to the anhydrous acid both the 2 eq. oxygen and the 1 eq. water, leaving the basic water unaltered.

BENZOYLE.

The term benzoyle denotes the hypothetical radical of a series of compounds which are produced from the volatile oil of the bitter

almond, or are connected with it by certain relations. The oil of bitter almonds itself is always a product of the decomposition of amygdaline, which exists in the kernels of most stone-fruits, and in the leaf of the *Prunus lauro-cerasus*, from which it may be obtained in a variety of ways. The formula of benzoyle is $C_{14}H_5O_2$; symb. Bz; eq. = 106.68.

Benzoyle cannot be said, strictly speaking, to be known in the separate state, and yet two compounds are known, the composition of which in 100 parts is the same as that of benzoyle. But there is every reason to believe that the group $C_{14}H_5O_2$, like cyanogen, plays the part of a simple body, combining with elementary substances, and with radicals in general. Thus compounds are known of this group with oxygen, hydrogen, chlorine, bromine, iodine, sulphur, cyanogen, and amide. We shall first describe these compounds, and then notice the numerous substances produced from the decomposition of these, especially of the hyduret of benzoyle, as well as those which appear to be formed by the coalescence of two or more molecules of compounds containing the group benzoyle, $C_{14}H_5O_2$. It will be seen that in these various ways an immense variety of new compounds has been obtained, the formation of which, when fully investigated, must necessarily shed much light on the nature of the processes carried on in the vegetable and animal kingdoms.

The following table contains the compounds in which the group $C_{14}H_5O_2$, or benzoyle, is admitted to exist as a compound radical.

	1 eq. Benzoyle.	Elementary Compound Radical.	Formulæ.
Benzoic Acid, Anhydrous	$C_{14}H_5O_2 + 1$ eq.	Oxygen	$C_{14}H_5O_3 = Bzo.$
Benzoic Acid, Hydrated.	$C_{14}H_5O_2 + 1$ eq.	O + 1 eq. Water	$C_{14}H_6O_4 = BzO.HO.$
Hyduret of Benzoyle	$C_{14}H_5O_2 + 1$ eq.	Hydrogen	$C_{14}H_6O_2 = BzH.$
Chloride of ditto.	$C_{14}H_5O_2 + 1$ eq.	Chlorine	$C_{14}H_5ClO_2 = BzCl.$
Bromide of ditto.	$C_{14}H_5O_2 + 1$ eq.	Bromine	$C_{14}H_5BrO_2 = BzBr.$
Iodide of ditto.	$C_{14}H_5O_2 + 1$ eq.	Iodine	$C_{14}H_5IO_2 = BzI.$
Sulphuret of ditto.	$C_{14}H_5O_2 + 1$ eq.	Sulphur	$C_{14}H_5SO_2 = BzS.$
Cyanide of ditto.	$C_{14}H_5O_2 + 1$ eq.	Cyanogen	$C_{14}H_5CyO_2 = BzCy.$
Benzamide	$C_{14}H_5O_2 + 1$ eq.	Amide	$C_{14}H_7NO_2 = BzAd.$

BENZOIC ACID.

Benzoic acid exists in gum benzoin, in dragon-blood, &c.; it is formed by the oxidation of the hyduret of benzoyle in the air, and by the decomposition of many compounds of benzoyle, of hippuric acid by acids, and of amygdaline by oxidizing reagents; by the action of potassa on the essential oils, cinnamon oil, &c.

Prep.—Gum benzoin, in the form of a coarse powder, either alone or mixed with an equal weight of sand, is spread upon the bottom of a round vessel of cast or plate iron, the sides of which should not be

more than three inches high. A sheet of dry bibulous paper is stretched tightly over the opening, and fastened to the sides of the vessel by a little paste. A hat made of thick paper, and of the common form of a man's hat, is made to cover the whole, and tightly tied to the sides of the vessel by a strong string. The vessel is now placed upon sand spread upon an iron plate, below which a fire is kept for 3—4 hours. The vapours of the sublimed benzoic acid pass readily through the pores of the bibulous paper, and are deposited in crystals upon the hat: the crystals are prevented from falling back into the iron vessel by the paper which closes its opening. (Mohr.) This is continued as long as a deposit of crystals is observed. Or in the following way, which is more productive, yielding the whole amount of the benzoic acid present in the benzoin. Benzoin is dissolved in strong alcohol, and to the hot solution there is added hydrochloric acid in quantity sufficient to precipitate the resin: the whole is then distilled. The benzoic acid passes over under the form of benzoic ether (benzoate of oxide of ethyle); and when the greater part of the liquid has been distilled off, water is added to the residue, and distilled as long as any ether passes over with it. When this ceases, the hot water remaining in the retort is filtered, and on cooling deposits part of the benzoic acid in crystals. The benzoic ether and all the distilled liquors are now treated with caustic potash, until all the ether is decomposed, and the solution, now containing benzoate of potash, is heated to boiling, and supersaturated with hydrochloric acid. On cooling it deposits the benzoic acid in crystals. A third and very excellent method is to boil the gum benzoin in powder with milk of lime, and to decompose the benzoate of lime, after separating the resin by filtration, with hydrochloric acid. Or hippuric acid is boiled for one quarter of an hour in nitric acid of sp. gr. 1.42, after which water is added, and the solution allowed to crystallize. The acid obtained from gum benzoin is purified either by a second sublimation, or being boiled in nitric acid, or by passing chlorine gas through its boiling aqueous solution.

The benzoic acid exists ready formed, and principally in a free state, in the gum benzoin, from which it is separated by sublimation. The method by distillation with alcohol depends on the ready formation and decomposition of benzoic ether, and has been explained above. Hippuric acid contains the elements of benzoic acid and glycocoll (sugar of gelatine). When boiled with acids the glycocoll enters into combination with the acid, while the benzoic acid is separated. (Dessaignes.)

Prop.—Benzoic acid crystallizes in soft whitescales, which are flexible, transparent, and of a mother-of-pearl lustre; or in hexagonal needles.

When pure it is inodorous, but if gently warmed it smells like gum benzoin; it has a slightly biting but sweetish taste, produces a burning sensation in the throat, reddens litmus feebly, fuses at 250° , sublimes at 300° , (an appearance of light is frequently observed in the dark,) boils at 462° , yielding a vapour of sp. gr. 4.27 ; it is not changed by chlorine or by being boiled with dilute nitric acid, but with strong nitric acid it yields a new acid, nitrobenzoic acid. It is dissolved by concentrated sulphuric acid, but falls upon the addition of water. When heated in open vessels, it emits white odoriferous fumes, which produce a scratching sensation in the throat, are very inflammable, and burn with a smoky flame, without leaving any residue. It is soluble in 200 parts of cold and 25 parts of boiling water; by boiling or evaporating its solution, a portion of the acid volatilizes with the aqueous vapour.

Its formula is $C_{14}H_5O_3 + aq.$, or $BzO + aq.$; eq. = 123.68 .

Benzoate of Ammonia.—Neutral benzoate of ammonia is prepared by dissolving benzoic acid in pure concentrated ammonia, by the aid of heat, till the latter is saturated, when it is allowed to cool. It forms feathery acicular crystals, which deliquesce in a moist air, and are soluble in absolute alcohol. Its formula is NH_4O, BzO . When benzoate of ammonia is distilled, there is obtained an oily fluid, called by its discoverer, Fehling, Benzonitrile. Its odour closely resembles that of hyduret of benzoyle. Its formula is $C_{14}H_5N$. Its formation is easily explained: $C_{14}H_5O_3 + NH_4O = C_{14}H_5N + 4HO$.

The acid salt is formed by boiling and exposing to spontaneous evaporation the neutral salt, when, with the loss of ammonia, it is deposited in large regular crystals.

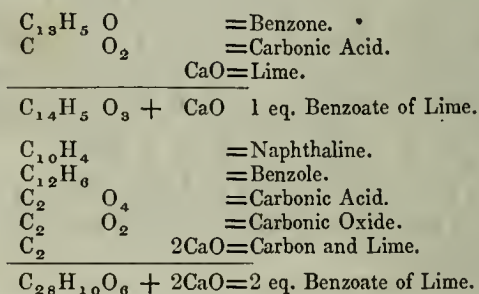
BENZOIC ACID AND METALLIC OXIDES.

The combination of benzoic acid with the metallic oxides is usually attended with the separation of the water of the hydrate; the soluble benzoates have a strong biting saline taste, and are decomposed by most other acids with the separation of benzoic acid; the same change occurs with the insoluble salts, when the acid which is added forms a soluble salt with the metallic oxide. According to Lecanu and Serbat, many of the benzoates, which are insoluble in water, are taken up by hot solutions of the acetate of potassa and soda, and of nitrate of soda; they are insoluble, on the contrary, in solutions of nitre, and of the sulphate of potassa and soda. The general formula for the benzoates of protoxides is MO, BzO , or M, BzO_2 . The benzoates of the alkalis are decomposed by the destructive distillation into carbonates, and a

variety of new products. Exposed to a red heat with an excess of hydrate of lime, the acid is decomposed into benzole and carbonic acid, which unites with the lime. Benzoates of potassa, soda, lithia, and magnesia are very soluble in water, and are with difficulty obtained in crystals.

Benzoates of baryta and strontia are sparingly soluble in cold, but more freely in boiling water, from which they are deposited in fine acicular crystals.

Benzoate of Lime.—Crystallizes with 1 eq. of water of crystallization in brilliant flexible needles or prisms, which require for solution 20 parts of cold, and somewhat less of boiling water. The products obtained by the distillation of this salt have been examined by Peligot. Two fluid products are thus obtained, first, benzene $C_{13}H_5O$, and benzole $C_{12}H_6$; then naphthaline $C_{10}H_4$; the residue is carbon and carbonate of lime, and carbonic acid is evolved. The explanation of the formation of benzene will at once be perceived, when it is mentioned that the anhydrous benzoate of lime contains the elements of benzene and carbonate of lime, or the elements of benzole, naphthaline, carbonic acid, carbonic oxide, and carbon.



Benzoate of Alumina.—Formed by adding the alkaline benzoates to the salts of alumina, a crystalline precipitate, which is redissolved by heat.

Benzoates of glucina, yttria, and zirconia, are sparingly soluble precipitates.

Benzoates of the protoxides of manganese and iron are soluble salts.

Benzoate of the Peroxide of Iron.—The neutral salt may be obtained in crystals, which are dissolved in water and alcohol with the separation of a basic salt; salts of the peroxide of iron, to the solutions of which so much ammonia has been added, that they lose their acid reaction but are not precipitated, form with the soluble benzoates of the alkalies a reddish-white, or, if an excess of ammonia has been used, a yellowish-brown precipitate, the latter of which is insoluble in water; it falls as a bulky gelatinous mass, which, when dried and exposed to

a red heat, leaves 25 per cent. of peroxide of iron. The first-mentioned reddish-white precipitate is decomposed by washing with hot water, when a soluble benzoate of the peroxide of iron is dissolved, and the yellowish-brown basic compound left; the decomposition is prevented by washing with a solution of sal-ammoniac. The benzoate of ammonia is sometimes used with the necessary precautions for separating peroxide of iron from the oxides of manganese, nickel, and zinc, which are not precipitated by it; it cannot be employed if the solution contain alumina, yttria, zirconia, or glucina, as these oxides also form very sparingly soluble salts with benzoic acid.

Its formula is $\text{Fe}_2\text{O}_3, 3\text{BzO}$.

Benzoate of Oxide of Copper.—This salt forms small bluish-green crystals, sparingly soluble. When distilled they yield in the residue salicylic acid, $\text{C}_{14}\text{H}_6\text{O}_6$, while the volatile product contains benzoic acid, and a crystallized body having the composition of the radical benzoyle, $\text{C}_{14}\text{H}_5\text{O}_2$.

Benzoate of Oxide of Lead.—A very sparingly soluble white crystalline powder, but soluble in acetic acid, from which it may be obtained in crystals; it contains 2 eq. water, the half of which is retained at 212° . A basic salt is obtained by precipitating a benzoate of the alkalies by the diacetate of lead in the form of a white anhydrous insoluble powder; it is composed of 3 eq. oxide of lead and 2 eq. anhydrous benzoic acid.

Benzoate of Oxide of Silver.—Dilute boiling solutions of a neutral benzoate of an alkali and nitrate of silver being mixed, yield, as they cool, soft flat needles of a white colour and strong lustre, and very similar to benzoic acid, which are anhydrous benzoate of oxide of silver; they blacken by exposure to light. Thrown down from concentrated solutions, it forms a curdy crystalline mass, which, dissolved in hot water, yields a dark-coloured solution owing to the reduction of silver; the salt is again deposited in the described form.

Its formula is AgOBzO .

HYDURET OF BENZOYLE.

Prep.—The essential oil obtained by the distillation of the bitter almond after maceration for some time with water, contains, besides the hyduret of benzoyle, benzoic acid, benzoine, and hydrocyanic acid: it is made into a thin paste by being mixed with hydrate of lime, chloride of iron, and water, and redistilled; the oil which passes over is freed from the admixture of water by standing over dry chloride of calcium.

Prop.—A colourless perfectly transparent limpid fluid, of a strong peculiar odour and burning taste; its sp. gr. is 1·043, refracts light strongly, boils at 356°. It is soluble in 30 parts of water, and mixes with alcohol and ether; its vapour is inflammable, and burns with a brilliant but smoky flame; it may be transmitted through red-hot glass tubes without decomposition. By exposure to the air it absorbs 2 eq. oxygen, and is converted into hydrated benzoic acid; the same change is effected, with the decomposition of water and the evolution of hydrogen, by exposing it to a high temperature with hydrate of potassa. Treated with an alcoholic solution of hydrate of potassa, it congeals in the course of a few moments to a mass of benzoate of potassa, which separates, when the alcohol is found to contain an oily substance not yet examined. If, however, hydrocyanic acid be added, or if the crude oil, which contains that acid, be used, the oil is soon changed into a solid mass, consisting chiefly of benzoine, a solid crystalline compound, isomeric or polymeric with the hyduret of benzoyle. By the action of chlorine or bromine, chloride or bromide of benzoyle, together with hydrochloric or hydrobromic acid, is formed; if water be present, there is formed at the same time either benzoate of hyduret of benzoyle, or benzoic acid. When gently heated with a solution of ammonia, it is converted into hydrobenzamide. It is dissolved by concentrated sulphuric acid with the aid of a gentle heat, but at a higher temperature the solution becomes first red and then black, and evolves sulphurous acid. It unites with anhydrous sulphuric acid, forming a peculiar acid, which is not precipitated by baryta. (Mitscherlich.) Nitric acid dissolves the hyduret of benzoyle, and converts it with difficulty into benzoic acid. It is poisonous when taken internally in the pure state.

Its formula is $C_{14}H_6O_2$, or $Bz + H$; eq. = 107·68.

CHLORIDE OF BENZOYLE.

Discovered by Wöhler and Liebig. It is prepared by passing a stream of chlorine gas through anhydrous hyduret of benzoyle as long as hydrochloric acid is evolved; the liquid which has acquired a yellow colour is then heated, to drive off all free chlorine, when it again becomes colourless.

Prop.—A colourless liquid of a peculiar unpleasant odour, which attacks the eyes, and has a sp. gr. = 1·196; the vapour is combustible and burns with a smoky flame tinged with green; it is slowly decomposed into hydrochloric and benzoic acids by cold water, more rapidly by hot water; added to an alkali, a benzoate of the alkali and a me-

tallic chloride are formed; it may be distilled unaltered from anhydrous lime or baryta, and dissolves sulphur and phosphorus without change; when brought into contact with the protochloride of phosphorus, a strong heat is developed, with the formation of the perchloride of phosphorus and a colourless oily substance which has not been further examined. It is decomposed by ammoniacal gas into benzamide and hydrochloric acid; by alcohol, into benzoate of oxide of ethyle and hydrochloric acid; it mixes without change with ether, and the bisulphuret of carbon.

Its formula is $C_{14}H_5O_2Cl$, or $BzCl$.

BROMIDE OF BENZOYLE.

Discovered by Wöhler and Liebig. Prepared like the chloride. It forms colourless scaly crystals, which become brown by exposure to the air; it is decomposed by water and the alkalies, in the same manner as the chloride; it dissolves without change in ether and alcohol.

Its formula is $C_{14}H_5O_2Br$, or $BzBr$.

IODIDE OF BENZOYLE.

Discovered by Wöhler and Liebig. It is prepared by distilling chloride of benzoyle and iodide of potassium, when it is obtained as a crystalline mass, coloured brown by an excess of iodine. When pure it forms colourless scaly crystals, which are very fusible and become brown in the air; it is acted upon by water and alkalies like the preceding compounds.

Its formula is $C_{14}H_5O_2I$, or BzI .

SULPHURET OF BENZOYLE.

Discovered by Wöhler and Liebig. Prepared by distilling the chloride of benzoyle with sulphuret of lead. It forms a yellow oil, which, when cooled, forms a soft crystalline mass, of a peculiarly unpleasant smell. It is hardly acted on by boiling water, but, when treated with solution of potash, it is slowly converted into benzoic acid and sulphuret of potassium. It is combustible, and dissolves unchanged in alcohol and ether.

Its formula is $C_{14}H_5O_2S$, or BzS .

CYANIDE OF BENZOYLE.

Discovered by the same chemists. Prepared by distilling chloride of benzoyle with bicyanide of mercury. A yellow oil, which, when rectified, becomes colourless. Its smell is similar to that of cinnamon, and it irritates the eyes violently. Its taste is pungent and sweetish, with an after-taste of prussic acid. It is inflammable.

Its formula is $C_{14}H_5O_2Cy$, or $BzCy$.

BENZAMIDE.

Discovered by the same. It is formed when any of the preceding combinations of benzoyle with supporters of combustion is acted on by dry ammoniacal gas; and it is also a product of the decomposition of hippuric acid by superoxide of lead. Chloride of benzoyle is saturated with dry ammonia; and the white solid mass produced, which is a mixture of sal-ammoniac and benzamide, is finely powdered, and well washed with cold water to remove the sal-ammoniac. The residue is dissolved in boiling water, and the benzamide crystallizes on cooling. Or hippuric acid is boiled with superoxide of lead, when carbonic acid is disengaged, and hippurate of lead and benzamide are formed, which remain dissolved. Sulphuric acid is now added, cautiously avoiding excess, and the whole is again boiled with a new portion of superoxide of lead. These operations are repeated till all the hippuric acid has been destroyed; and the liquid, when freed from lead, yields crystals of benzamide by evaporation. Chloride of benzoyle with ammonia produces benzamide and free hydrochloric acid, which is converted into sal-ammoniac by the ammonia in excess; $BzCl + AdH = BzAd + HCl$. Hippuric acid contains the elements of fumaric acid and benzamide. When boiled with superoxide of lead, the organic acid is converted into carbonic acid and water, while the benzamide is liberated.

Benzamide forms right rhombic prisms, or four-sided pearly scales. A concentrated hot solution by slow cooling forms a soft mass of minute crystals, which spontaneously pass into scales of considerable size, after some time. The crystals are colourless and transparent, and melt at about 240° . At a higher temperature they are volatilized, producing an inflammable vapour.

Benzamide is sparingly soluble in cold water; freely and without change in hot water. It is also soluble in alcohol and ether. Alkalies and acids, water being present, decompose benzamide, with the

production of benzoic acid and ammonia. When benzamide is gently heated with anhydrous baryta, a violent reaction takes place, with disengagement of heat. Benzoate of baryta is formed; ammonia is disengaged; and a colourless oily liquid distils over, consisting chiefly of benzole.

The formula of benzamide is $Bz + NH_2$, or $BzAd$.

FORMOBENZOIC ACID; OR, FORMIATE OF HYDURET OF BENZOYLE.

Discovered by Winkler. Prepared by dissolving commercial oil of bitter almonds in water, adding hydrochloric acid, and evaporating in a gentle heat. The dry residue, consisting of formobenzoic acid and sal-ammoniac, is treated with ether, which dissolves the new acid. It is obtained in crystals by the evaporation of the ether, and is decolorized by animal charcoal.

It forms a white granular powder, imperfectly crystallized, or a scaly crystalline mass, which has a strong sour taste, and a faint odour of almonds. When heated, it melts, with disengagement of water, into an oily fluid, which at a higher temperature is decomposed, with a pleasant odour, like that of hawthorn blossom, and leaves behind a bulky coal. It is very soluble in water, alcohol, and ether; and decomposes, with the aid of heat, the salts of acetic, carbonic, and benzoic acids. Its aqueous solution, heated with superoxide of manganese, is resolved into carbonic acid and hyduret of benzoyle. The same result ensues from the action of nitric acid or of chlorine.

The formobenzoic acid is produced, in the process above described, in the following manner. The commercial oil of bitter almonds contains hydrocyanic acid mixed with the pure oil or hyduret of benzoyle. In contact with a strong mineral acid and water, the hydrocyanic acid (see that article) is resolved into formic acid and ammonia; the former of which, while nascent, unites with the hyduret of benzoyle to produce the new acid. Oxidizing agents, by the addition of 2 eq. oxygen, convert the formic acid into carbonic acid and water, while the hyduret of benzoyle is set free.

The formula of the formobenzoic acid is $C_2HO_3 + C_{14}H_6O_2 + aq.$, or $FoO_3 + BzH + aq.$

FORMOBENZOIC ACID AND METALLIC OXIDES.

Metallic oxides readily combine with this acid, equivalent to equivalent, forming neutral salts. Those with potash and soda are very soluble, and crystallize with difficulty. Formobenzoate of baryta

crystallizes in small, hard, transparent prisms. The salt of silver obtained by mixing solutions of formobenzoate of ammonia and nitrate of silver, appears as a heavy white crystalline and granular precipitate, which is soluble in hot water, and crystallizes on cooling in small anhydrous scales.

BENZOATE OF HYDURET OF BENZOYLE.

Discovered by Robiquet and Boutron Charlard. It is obtained by saturating common oil of bitter almonds with moist chlorine gas. The liquid, after standing for some time, is converted into a semi-solid mass of crystals, which are to be washed with cold ether. It forms a dazzling white crystalline powder; or short, thin, transparent, and very brilliant four-sided prisms, insoluble in water, soluble in alcohol, slightly soluble in ether. It dissolves easily in alcohol saturated with caustic potash, forming a colourless solution, out of which, after a time, benzoate of potash crystallizes. It melts when heated, and may be sublimed without decomposition. Its formation by the action of moist chlorine on the oil is thus explained: the chlorine converts a part of the oil into hydrated benzoic acid, which, in the nascent state, combines with another portion of the oil. $BzH + 2HO + Cl_2 = BzO,HO + 2HCl$.

Its formula is $C_{14}H_6O_4 + 2(C_{14}H_6O_2)$, or $BzO,HO + 2BzH$.

HIPPURIC ACID.

Discovered by Liebig. Occurs, combined with soda or ammonia, in the urine of the gramivora, such as the horse and cow. It is obtained from the fresh urine by boiling it with an excess of milk of lime, straining, boiling down the clear liquid to $\frac{1}{10}$ th of its original volume, adding so much hydrochloric acid as to produce an acid reaction, and setting it aside to rest, when coloured hippuric acid is deposited in crystals. (Gregory.) Liebig has lately detected it in human urine.

When decolorized, which is best effected by boiling the coloured crystals with milk of lime, and decomposing the filtered solution by muriatic acid, a process which may be repeated if necessary, the hydrate of lime retaining the colouring matter, the hippuric acid forms long, transparent or milk-white four-sided prisms, acuminate on two faces; having a slight bitterish taste. It reddens litmus strongly, and melts when heated, concreting into a crystalline mass on cooling. A high temperature decomposes it, when benzoic acid and benzoate of ammonia distil over in red oily drops, which have a strong and agreeable

odour of Tonka beans, and soon become solid. The smell belongs to a new oily product. Towards the end of distillation, hydrocyanic acid is disengaged, and a porous coal is left. Hippuric acid is soluble in 400 parts of cold water, but is easily dissolved at a boiling heat. In oil of vitriol it dissolves without colour by the aid of a gentle heat; in a higher temperature the acid is blackened, benzoic acid sublimes, and sulphurous acid is disengaged. Nitric acid converts it easily into benzoic acid: the same change is effected by boiling with muriatic acid. If gently heated with hyperoxide of manganese and sulphuric acid, it is resolved into carbonic acid, ammonia, and benzoic acid. Boiled with hyperoxide of lead, it yields benzamide and carbonic acid.

If the urine of the horse or cow be left to itself for a long time, or evaporated at a boiling temperature, it yields not a trace of hippuric acid, but only benzoic acid. The same thing occurs if the animal be hard worked; hence, to obtain hippuric acid, the urine of stall-fed animals is taken.

The formula of the hippuric acid is $C_{18}NH_8O_5 + aq.$ It may be represented as benzamide $C_{14}NH_7O_2$, combined with equisetic or fumaric acid C_4HO_3 ; or as hyduret of benzoyle $C_{14}H_6O_2$, combined with hydrocyanic acid C_2NH , and formic acid C_2HO_3 . Either of these rational formulæ will explain its ready conversion into benzoic acid.

Rational formula of hippuric acid, $BzAd + C_4HO_3 + aq.$, or $B3H + HCy + FoO_3$.

Dessaignes has recently shewn, that, when hippuric acid is boiled for a long time with hydrochloric acid, it is entirely decomposed into benzoic acid and sugar of gelatine or glycocoll. In fact, if to

Hippuric Acid . . .	$C_{18}NH_8O_5$
we add 2 eq. water . .	H_2O_2
and from the sum . .	$C_{18}NH_{11}O_8$
subtract Benzoic Acid .	$C_{14}H_6O_4$
there will remain . .	$C_4NH_5O_4$; and

this is the formula of glycocoll, as corrected by Gerhardt from the analyses of Mulder and Boussingault, and as confirmed by the recent researches of Horsford. Other mineral acids produce the same result. In this beautiful decomposition the sugar of gelatine, which is an organic base, and, according to Dessaignes, is very analogous to urea, remains combined with the hydrochloric acid, and forms a salt, which may be obtained in beautiful crystals after separating the benzoic acid.

HIPPURIC ACID AND METALLIC OXIDES.

Hippuric acid forms soluble and crystallizable salts with the alkalies and alkaline earths. Its salts with the oxides of the heavy metals, except that with peroxide of iron, are sparingly soluble in cold, more easily in hot water, and crystallizable. The hippurate of peroxide of iron has the colour and external characters of the benzoate. The hippurate of silver is anhydrous. All the hippurates are decomposed by acids, which separate the hippuric acid: these salts, melted with an excess of hydrate of lime or of potash, give off ammonia and an oily liquid (benzole).

PRODUCTS OF THE DECOMPOSITION OF THE COMPOUNDS OF BENZOYLE.

HYPOSULPHOBENZOIC ACID.

Synon. Sulphobenzoic Acid. A bibasic acid, discovered by Mitscherlich. It is prepared by adding, to a solution of acid hyposulphobenzoate of baryta, diluted sulphuric acid, till the baryta is entirely precipitated. The filtered solution is evaporated, at first over the open fire, and at last in the vacuum of an air-pump with the aid of sulphuric acid, when the hyposulphobenzoic acid crystallizes. In the formation of this acid by the action of anhydrous sulphuric acid on benzoic acid, 2 eq. sulphuric acid and 1 eq. benzoic acid produce water and hyposulphobenzoic acid; $C_{14}H_5O_3 + 2SO_3 = C_{14}H_4O_3 + S_2O_5 + HO$.

Formula, $C_{14}H_4O_3 + S_2O_5 + 2 aq$.

It forms a colourless crystalline mass, deliquescent in a moist atmosphere, having a strong sour taste. It bears a heat of 300° without decomposition; and is not decomposed by boiling with hydrochloric acid nor by nitric acid. Solutions of barytic salts cause in its solution a precipitation of acid hyposulphobenzoate of baryta, in crystals, on cooling, if the solution be strong.

HYPOSULPHOBENZOIC ACID AND METALLIC OXIDES.

This acid forms two series of salts. The neutral salts contain 2 eq. metallic oxide; the acid salts, dried at 212° , 1 eq. metallic oxide and 1 eq. water. All the salts of this acid, when melted with an excess of hydrate of potash, leave a residue containing a mixture of sulphate, sulphite, and carbonate of potash.

Acid Hyposulphobenzoate of Baryta.—The vapours of anhydrous sulphuric acid are conducted into a dry receiver, containing crystallized benzoic acid, and surrounded with cold water. The sulphuric acid combines with the benzoic acid, forming a translucent mass like turpentine. This mass is mixed with water, as soon as the crystalline structure of the benzoic acid has disappeared. After the acid liquid, by standing, has deposited any excess of benzoic acid, it is neutralized by carbonate of baryta, evaporated and mixed with hydrochloric acid, when on cooling it deposits the acid hyposulphobenzoate of baryta in crystals. It may be rendered perfectly colourless by animal charcoal, and purified from muriatic acid by repeated crystallization. It forms transparent, oblique rhombic prisms, generally twin crystals, soluble in 20 parts of cold water and much less of boiling water. It contains 3 at. water of crystallization, which is expelled by a heat of 212° .

Neutral Hyposulphobenzoate of Baryta is obtained by boiling the preceding salt with carbonate of baryta: it is more soluble than the acid salt; difficultly crystallizable, and bears a heat of 630° without decomposition.

Neutral Hyposulphobenzoate of Lead is obtained by mixing a hot solution of the last salt with one of acetate of lead. It crystallizes on cooling in fine white silky needles arranged in radiated tufts; very sparingly soluble in cold, more easily in hot water. It contains 2 at. water of crystallization.

BROMOBENZOIC ACID.

A bibasic acid, discovered by Peligot. To prepare this acid, dry benzoate of silver and bromine, the latter in an open tube, are introduced into a stoppered bottle, which is then closed, and the whole left to itself in the ordinary temperature. The vapour of bromine rising out of the tube is absorbed by the salt, which is decomposed thereby. As soon as the red vapours of unabsorbed bromine are seen in the bottle, the reaction is complete. The mass is now treated with ether, which dissolves bromobenzoic acid, and leaves bromide of silver undissolved. By the evaporation of the ether, the acid is obtained in the form of a brown oily matter, which after a time becomes solid and crystalline. It commonly contains a little benzoic acid and an oily matter, to which latter its colour is owing. To purify it, it is combined with potash, the solution decolorized by animal charcoal, and the salt then decomposed by nitric acid, when pure bromobenzoic acid separates. In this process, when bromine acts on benzoate of silver, both the benzoic acid and the oxide of silver are decomposed. From 2 at. oxide of sil-

ver, 2 at. oxygen pass over to the elements of the acid. Bromide of silver is formed, 1 eq. hydrogen out of 2 at. benzoic acid unites with 1 eq. bromine; and is separated as hydrobromic acid. Finally 1 eq. bromine takes the place of the hydrogen. $(C_{28}H_{10}O_8 + Ag_2) + Br_4 = (C_{28}H_9BrO_8) + 2AgBr + HBr.$ The anhydrous bromobenzoic acid which is here formed combines with 2 at. water when separated from its salts by a stronger acid.

Its formula is $C_{28}H_9BrO_8 + 2 aq.$

It forms a colourless crystalline mass, fusible at 212° , subliming at 480° , with a partial decomposition, and leaving a residue of carbon. It is sparingly soluble in water, very soluble in alcohol, ether, and pyroxylic spirit. It is inflammable, and burns with a smoky flame edged with green. Its solutions, added to nitrate of silver, produce no precipitate of bromide of silver.

BROMOBENZOIC ACID AND METALLIC OXIDES.

Bromobenzoic acid forms soluble salts, some of which crystallize, with the alkalies, alkaline earths, and the oxides of zinc, cobalt, nickel, mercury, and silver; and sparingly soluble salts with oxides of lead and copper and protoxide of mercury. The bromobenzoate of peroxide of iron is insoluble, and resembles the benzoate of that oxide.

BENZOLE (BENZINE).

Syn. Phène, Benzéne. First discovered by Faraday among the products of the destructive distillation of organic substances; afterwards noticed by Mitscherlich as the chief product of the decomposition of crystallized benzoic acid by hydrate of lime at a high temperature.

To prepare it, 1 part of crystallized benzoic acid, intimately mixed with 3 parts of slaked lime, is subjected to distillation. The oily liquid obtained is purified by re-distillation with water, or with hydrate of lime and dry lime.

It is a clear colourless liquid of a peculiar, ethereal, agreeable odour; boils at 186° ; its sp. gr. in the liquid form is 0.85; in the form of vapour, 2.738 at 60° . It freezes at 32° into a crystalline mass resembling loaf-sugar, which melts again at 44° . It is insoluble in water, soluble in ether and alcohol, not altered by hydrated acids, not acted on by potassium, which retains its lustre in the liquid. From its sp. gr. in the state of vapour, it appears to contain 3 vol. hydrogen and 3 vol. carbon vapour. Its formula is C_2H . But it is probable that

the formula $C_{12}H_6$ represents its true atomic weight. It is polymeric with formyle, a hypothetical radical hereafter to be described.

Its production from benzoic acid is thus easily explained; for if from 1 at. crystallized benzoic acid we take away (by the lime) 2 at. carbonic acid, benzole remains. $C_{14}H_6O_4 - C_2O_4 = C_{12}H_6 = 6C_2H$.

PRODUCTS OF THE DECOMPOSITION OF BENZOLE.

Sulphobenzide.—Discovered by Mitscherlich. Benzole and anhydrous sulphuric acid are brought together, when they form a viscid liquid, without special signs of decomposition. The compound dissolves in a small quantity of water, but by the addition of more water sulphobenzide is precipitated, which may be obtained in crystals by solution in ether and spontaneous evaporation. Here 1 at. sulphuric acid and 1 at. benzole produce 1 at. water and 1 sulphobenzide.

It is a colourless, inodorous, indifferent body, melts at 212° , and sublimates without decomposition at a higher temperature.

Its formula is $C_{12}H_5SO_2$.

Hyposulphobenzidic Acid.—This acid is contained in the liquid from which, in the above process, the sulphobenzide has separated. It is also formed by dissolving sulphobenzide in oil of vitriol, and by the action of the fuming sulphuric acid on benzole. It may be considered as composed of oil of vitriol and sulphobenzide, which explains its formation. It is obtained pure by decomposing the hyposulphobenzidate of copper by sulphuretted hydrogen. It forms a very sour liquid, which crystallizes when evaporated to the consistence of syrup, and bears a heat of nearly 400° without decomposition.

Its formula is $C_{12}H_5S_2O_5$ in its salts.

Hyposulphobenzidate of Baryta.—A soluble salt, crystallizing indistinctly. It is obtained by dissolving in fuming oil of vitriol as much benzole as it will take up, mixing the solution with water, filtering to separate the sulphobenzide, and neutralizing the liquid with carbonate of baryta. A second filtration separates the sulphate of baryta which is formed at the same time, and the filtered liquid contains the barytic salt in question.

Hyposulphobenzidate of Copper.—The solution of the preceding salt is accurately precipitated by sulphate of copper, and the sulphate of baryta separated by filtration. The filtered liquid, being evaporated, yields on cooling large regular crystals of hyposulphobenzidate of copper. This salt contains water of crystallization, which it loses at 340° . It may be heated to 430° without decomposition.

NITROBENZIDE.

Discovered by Mitscherlich. Syn. Nitrobenzole. Prepared by adding to warm, red, and fuming nitric acid as much benzole as it can dissolve, adding water, and allowing the whole to cool. Nitrobenzide precipitates. It is at 60° a yellow liquid of an intensely sweet taste, and an odour like that of cinnamon. It boils at 415° ; sp. gr. of the liquid 1.209, of the vapour 4.294. It crystallizes at 38° in needles, insoluble in water, soluble in alcohol and ether. Nitrobenzide is soluble in diluted acids, from which it is precipitated by water. It is decomposed by oil of vitriol, but not by alkalis.

Its formula is $C_{12}H_5NO_4$; and it may be regarded as benzole, in which 1 eq. hydrogen has been replaced by 1 eq. nitrous acid, without change of type, so that benzole $C_{12}H_6$ corresponds to nitrobenzole $C_{12}\left\{\begin{smallmatrix} H_5 \\ NO_4 \end{smallmatrix}\right\}$. Zinin discovered that nitrobenzole, when acted on by sulphuret of ammonium, lost all its oxygen, and taking up 2 eq. of hydrogen, was converted into a basic oil, which he called benzidam, but which was soon found to be aniline, a very remarkable base, to be hereafter described. The formula of aniline is $C_{12}H_7N$, and it may be considered as benzole, in which 1 eq. hydrogen is replaced by 1 eq. amide $C_{12}\left\{\begin{smallmatrix} H_5 \\ NH_2 \end{smallmatrix}\right\}$.

BINITROBENZIDE.

Syn. Dinitrobenzole.—When benzole or nitrobenzole is heated with a mixture of strong nitric and sulphuric acids, it is quickly changed into dinitrobenzole, which on cooling is deposited in crystals. In this compound the type of benzole is still retained, but 2 eq. of hydrogen are replaced by nitrous acid, so that it is best represented as $C_{12}\left\{\begin{smallmatrix} H_4 \\ 2NO_4 \end{smallmatrix}\right\}$.

Hoffmann and Muspratt have shewn that dinitrobenzole, acted on by sulphuretted hydrogen and ammonia, yields a new base analogous to aniline, which they have called nitraniline. Its empirical formula is $C_{12}N_2H_6O_4$; and it is aniline in which 1 eq. of hydrogen is replaced by 1 eq. of nitrous acid; thus, aniline $C_{12}H_7N$ corresponds to nitraniline $C_{12}\left\{\begin{smallmatrix} H_6 \\ NO_4 \end{smallmatrix}\right\}N$. This compound is very remarkable, both from its mode of formation and its retaining the basic characters of its type aniline, while it contains 1 eq. of nitrous acid. We shall return to this subject under aniline.

AZOBENZIDE.

Discovered by Mitscherlich. Nitrobenzide is dissolved in alcohol, and heated with solid hydrate of potash: the red solution which is formed is then distilled. At first alcohol, then azobenzide distils over, and they are collected separately. It forms large red crystals, fusible at 150° , boiling at 380° .

Its formula is $C_{12}H_5N$. It is formed from nitrobenzide, along with aniline and oxalic acid, according to Hoffmann, who has studied the reaction. 2 eq. of nitrobenzole and 1 eq. of alcohol contain the elements of 1 eq. aniline, 1 eq. azobenzide, 2 eq. oxalic acid, and 2 eq. water. But the action seems to be even more complicated than this, for other products, not fully studied, are likewise formed.

CHLORIDE OF BENZOLE.

Discovered by Mitscherlich and Peligot. It is formed by the action of chlorine gas on benzole aided by the sun's rays. The benzole changes into a crystalline mass of chloride of benzole, which is a colourless solid, fusible at 270° , and boiling with partial decomposition at 550° . It is insoluble in water, soluble in alcohol and ether, and crystallizes easily from the latter solution.

Its formula is C_2HCl , or $C_{12}H_6Cl_6$.

CHLOROBENZIDE.

Discovered by Mitscherlich. When the preceding substance is distilled, half of its chlorine and hydrogen are separated, especially with the aid of an alkali, such as hydrate of lime. It forms a colourless oily liquid, which boils at about 410° . Sp. gr. of the liquid at 45° , 1.457; of the vapour, 6.37.

Its formula is $C_{12}H_3Cl_3$, and it is benzole in which half the hydrogen is replaced by chlorine; $C_{12}\left\{\begin{matrix} H_3 \\ Cl_3 \end{matrix}\right\}$. The preceding compound is probably a compound of this with 3 eq. hydrochloric acid.

Benzole forms corresponding compounds with bromine.

BENZONE.

Discovered by Mitscherlich and Peligot. Syn. Carbobenzdic of Mitscherlich. It is produced in the distillation of benzoate of lime.

(See that salt.) To obtain it, the raw product of the distillation of benzoate of lime is heated, first in the water-bath, and then gradually up to 920° , as long as benzole passes over. The residue is then distilled separately. The product is now benzene, holding in solution a certain quantity of naphthalene, which, by exposure to a cold of -5° , crystallizes out, and leaves, according to Peligot, pure benzene. Benzene is a colourless or pale yellow, viscid, oily liquid, heavier than water. It is decomposed by sulphuric acid or chlorine, but not by nitric acid or caustic potash.

Its formula is $C_{13}H_5O$. It may be derived from benzene and carbonic acid, by the removal of the elements of water; $C_{12}H_6 + CO_2 = (C_{12}H_5 + CO) + HO$. It may be regarded as benzene in which 1 eq. hydrogen is replaced by 1 eq. carbonic oxide $C_{12}\left\{\begin{matrix} H_5 \\ CO \end{matrix}\right\}$.

PRODUCTS OF THE TRANSFORMATION OF HYDURET OF BENZOYLE.

When the crude oil of bitter almonds is dissolved in absolute alcohol, and a current of ammonia passed through the solution, or when the oil is left for a long time in contact with very strong aqua ammoniac, there are formed several new products, of which three, namely, *Hydrobenzamide*, *Benzhydramide*, and *Amarine*, are isomeric or polymeric. When the pure hyduret is used instead of the crude oil, hydrobenzamide is the chief product. The other products of this reaction are Benzoic acid, Azobenzoyl, and Azotide of benzoyl or Nitrobenzoyl.

Hydrobenzamide is obtained in large and regular crystals by solution in alcohol and spontaneous evaporation. It forms regular octahedrous or rhombic prisms, tasteless, inodorous, and colourless; melting at 230° , and burning with a smoky flame. When distilled, it is decomposed, giving rise to new products: it is insoluble in water, soluble in alcohol, sparingly soluble in ether. The alcoholic solution, by boiling, is resolved into ammonia and hyduret of benzoyl. When heated with hydrochloric acid, it is quickly and easily resolved into hyduret of benzoyl and sal-ammoniac. Solution of potash, when long boiled with it, converts it into amarine without change of weight, amarine being polymeric with hydrobenzamide. It is produced by the action of 2 eq. ammonia on 3 at. of hyduret of benzoyl, forming 1 at. hydrobenzamide and 6 at. water. $3(C_{14}H_6O_2 + 2(NH_3)) = 6HO + (C_{42}H_{18}N_2)$; which last is the formula of hydrobenzamide.

Laurent, to whom we owe the discovery of these remarkable compounds, has recently suggested another view of the constitution of hy-

drobenzamide. He considers that its easy transformation, above mentioned, into hyduret of benzoyle and ammonia, indicates that it belongs to the same series as the hyduret, and consequently contains only 14 eq. of carbon. But in this case its formula becomes $C_{14}H_6N_{\frac{2}{3}}$; and to avoid fractions, Laurent supposes that nitrogen has 2 equivalents, a supposition which has also been made with regard to some other elements, and which is not so improbable as it may at first appear to be. If one of its equivalents be $N = 14$, and the other $Az = \frac{14}{3} = 4.666$, then this compound, assuming 14 eq. of carbon, becomes $C_{14}H_6Az_2$, which Laurent proposes to call azotide of benzène, corresponding to the hyduret, $C_{14}H_6O_2$, which he calls oxide of benzène, benzène being, of course, $C_{14}H_6$.

Benzhydramide has the same composition, in 100 parts, as hydrobenzamide. When the above-mentioned resinous mass is boiled with ether, both these substances are dissolved. By continued boiling, the hydrobenzamide is resolved into ammonia and hyduret of benzoyle. The benzhydramide crystallizes on cooling, mixed with azobenzoyl. Boiling alcohol dissolves the former, leaving the latter undissolved; and the benzhydramide is purified by repeated crystallization out of alcohol. It crystallizes in rectangular or six-sided prisms, melts when heated into a transparent liquid, which when cold is not crystalline. A stronger heat decomposes it. It is not altered by boiling hydrochloric acid. The crystals are commonly mixed with others, whose form and reactions seem to indicate that they are a different substance.

The formula of benzhydramide is believed to be $C_{42}H_{18}N_2$, being the same as the first of the two above mentioned for hydrobenzamide. It is probably formed by the coalescence of 3 eq. of hydrobenzamide, or by the action, as above explained, of 2 eq. ammonia on 3 eq. of the hyduret.

Amarine, $C_{42}H_{18}N_2$, is dissolved out of the mixed product of the action of ammonia on the hyduret by hydrochloric acid, and being a base, is precipitated by the addition of ammonia. It is also formed when hydrobenzamide is long boiled with caustic potash. If hydrobenzamide be $C_{14}H_6Az_2$, then 3 eqs. coalesce to form 1 eq. of amarine, $C_{42}H_{18}N_2$. It forms, when pure, fine needles, colourless, and at first tasteless, but having after a time a bitter taste. It is insoluble in water, soluble in hot alcohol, fusible and volatile at a high temperature. It exhibits all the characters of an organic base, forming crystallizable salts with sulphuric and nitric acids, and a crystallizable double salt with chloride of platinum. Its formation is very interesting because it so much resembles the natural organic bases, containing, like them, a large number of equivalents of carbon, and,

with its salts, possessing the bitter taste so generally found in that class of compounds.

Benzimic acid is formed along with the preceding bodies, and, when water is added to the mass formed by the action of ammonia on the hyduret, is dissolved in combination with ammonia. By the addition of hydrochloric acid it is thrown down in minute white needles, very sparingly soluble in water, and sparingly soluble even in alcohol. Laurent, who discovered it, has not yet given an analysis of it.

Azobenzoyl.—The residue of the preparation of benzhydramide contains azobenzoyl and nitrobenzoyl. This residue is boiled with 100 parts of alcohol, which on cooling deposits crystals of azobenzoyl. It forms a fine white crystalline powder, decomposable by heat.

Its formula is $C_{42}H_{15}N_2$; according to which it may be formed by the action of 3 at. benzoyl and 2 eq. ammonia. $3(C_{14}H_5O_2) + 2NH_3 = 6HO + C_{42}H_{15}N_2$.

Nitrobenzoyl.—The insoluble residue of the preparation of the last substance is nitrobenzoyl. It forms a white tasteless powder, nearly insoluble in alcohol. By alkalis it is converted into another crystalline body, not examined. Its formula is $C_{14}H_5N$.

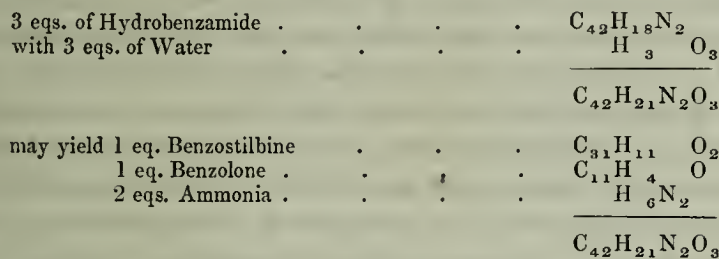
Lophine.—When hydrobenzamide (azotide of benzène) is distilled, it yields at first ammonia, then a fragrant oil, and there is left in the retort a mass which requires a strong heat to volatilize it. This mass is poured out, and is acted on by ether, which dissolves out a substance not yet further described, leaving undissolved the lophine. It is dissolved in alcohol with the aid of hydrochloric acid, and being a base, is precipitated by ammonia. It forms white silky crystals, very sparingly soluble in alcohol and ether, insoluble in water. Naphtha and oil of turpentine dissolve it rather better, but its best solvent is an alcoholic solution of potash. Its salts are soluble in alcohol. It has, like amarinc, all the characters of an organic base. Its formula is $C_{46}H_{16}N_2$.

By the action of hot nitric acid it yields an orange yellow crystalline compound, *nitrolophyle*, in which 3 eq. of hydrogen are replaced by 3 eq. of nitrous acid. Its formula is $C_{46}\left\{\begin{matrix} H_{13} \\ 3NO_4 \end{matrix}\right\}N_2$.

Benzostilbine.—When hydrobenzamide, according to Rochleder, is heated with fused potash till the mass acquires the aspect of gamboge, there is formed a new body, benzostilbine, along with a yellow oil. Alcohol dissolves both; but when the oil is decomposed by means of chlorine, in the alcoholic solution, the benzostilbine is deposited in small silvery crystals. Its formula is $C_{31}H_{11}O_2$. It is insoluble in water, and sparingly soluble in alcohol. Oil of vitriol dissolves it

with a blood-red colour, but the addition of water precipitates it unchanged.

Benzolone.—When, in the above process, hydrobenzamide is heated with fused potash till the mass becomes blackish brown, another new body, benzolone, is the chief product. The mass is dissolved in oil of vitriol, to which it gives a fine red colour, and the addition of weak alcohol now precipitates the benzolone in small crystals. Its formula is $C_{11}H_4O$.



But it is probable that benzostilbine is first formed as above, and then decomposed by the increased heat, yielding benzolone. The elements of benzostilbine correspond to 2 eq. of benzolone, 9 eq. of carbon, and 3 eq. hydrogen. Hydrogen and carburetted hydrogen are given off, and it would appear that part of the carbon is oxidized at the expense of water, the hydrogen of which is expelled, and that the carbonic acid thus formed unites with the potash.

Amarone.—This compound is formed along with lophine when nitrobenzoyle is distilled. When the lophine is dissolved by alcohol and hydrochloric acid, the amarone is left. It is purified by solution in hot naphtha, which on cooling deposits it in crystals. Its formula is said by Laurent to be $C_{32}H_{11}N$, and it is therefore probably derived from 3 eq. of nitrobenzoyle; but its formation is not yet fully understood. Its composition is that of a basic compound; but if a base, it is a very feeble and doubtful one.

Benzimide.—Discovered by Laurent. An ingredient of the raw oil of bitter almonds, from which it separates under certain circumstances. It forms white, inodorous, pearly needles and lamellæ, very light and flocky; insoluble in water, very sparingly soluble in alcohol and ether, rather more so in pyroxylic spirit. It melts at about 300° ; is inflammable, burns with a red, smoky flame; and is dissolved and decomposed by nitric, hydrochloric, and sulphuric acids, the latter of which is coloured by it dark indigo-blue, or green if moisture be present. According to Laurent, it is resolved by acids into ammonia and benzoic acid; but, for want of material, his experiments are not to be considered decisive.

Its formula is $C_{23}H_{11}O_4N$. Nothing is known of the way in which it is formed; but if the formula be correct, it may be considered as anhydrous benzoate of ammonia, *minus* 2 at. of water.

Benzoine.—*Syn. Oxide of Stilbene.*—Discovered by Robiquet and Boutron Charlard. It is produced by the contact of alkalies with the commercial oil of bitter almonds, but not with the pure hyduret of benzoyl. When the raw oil is distilled with hydrate of lime and protochloride of iron, the residue is a mixture of benzoine with lime and hydrated protoxide of iron. It is treated with hydrochloric acid, which dissolves the iron and lime; and the undissolved benzoine is purified by solution in alcohol with the aid of animal charcoal. Or the raw oil is dissolved with the aid of heat in lime or baryta water, and the solution, in a stoppered bottle, is kept for several hours at the temperature of 212° , when it becomes filled with fine, snow-white, flaky crystals, which, if dissolved in hot alcohol, are deposited in a state of purity on cooling. The best method of preparing it consists in mixing a solution of caustic potash in alcohol, with an equal volume of raw oil of bitter almonds. After a little time the mixed liquids become apparently solid from the quantity of small crystals of benzoine formed in them; these must be purified by crystallization from alcohol. They form hard, transparent, colourless, very brilliant prisms, without smell or taste; melting at about 230° , volatilizing unchanged at a higher temperature; inflammable, burning with smoke; insoluble in cold, little soluble in hot water, more soluble in boiling than in cold alcohol. Benzoine is soluble in oil of vitriol with a violet-blue colour; if the solution be heated, becoming brown, green, and at last black with disengagement of sulphurous acid. Heated with nitric acid it is converted into benzil. It is insoluble in aqueous solutions of the alkalies. If melted with hydrate of potash, benzoate of ammonia is formed, with disengagement of hydrogen gas. An alcoholic solution of potash dissolves it with a violet-blue colour; and if the solution be boiled, it passes into benzilic acid. Its vapour, passed through a red-hot glass tube, is converted into an oily substance with the odour of bitter almonds (hyduret of benzoyl). It is decomposed by bromine. Chlorine gas, when made to act on melted benzoine, deprives it of some hydrogen, and converts it into benzil.

The part which hydrocyanic acid plays in the production of benzoine by the action of alkalies on hyduret of benzoyl is still obscure. It is certain that benzoine cannot be obtained from pure hyduret of benzoyl; but that it appears after a few hours, when a little hydrocyanic acid is added to a hot solution of the pure hyduret in barytic water, if the solution be kept hot. After the separation of the ben-

zoinc, the liquid contains ammonia and benzoic acid, with a mere trace of formobenzoic acid.

Benzoine has the same composition in 100 parts as the hyduret of benzoyle, but there is reason to believe that it is formed by the coalescence of 2 eqs., and that its formula is, therefore, $C_{28}H_{12}O_4$. Laurent is now disposed to consider it as an oxide of stilbène, stilbène being a carbo-hydrogen, the formula of which is $C_{28}H_{12}$.

When ammonia is made to act on benzoine it gives rise, as with the hyduret, to several new products; but, hitherto, only two of these have been purified and described by Laurent, who found it very difficult to separate them from the accompanying products.

Benzoinamide.—*Syn. Hydrobenzoinamide.*—This body is a white tasteless powder, soluble in alcohol, and crystallizable. It is volatile without decomposition. Its formula is supposed by some to be $C_{42}H_{18}N_2$, which is that of benzhydramide. It is, however, most probable that these two compounds really have different formulæ, that is, are polymeric only, although at present we do not know the precise difference between them. Laurent considers benzoinamide to be an azotide of stilbène, $C_{28}H_{12}Az_4$, corresponding to benzoine, which is the oxide.

Benzoinam.—This, the second compound obtained by the action of ammonia on benzoine, is purified by solution in alcohol with hydrochloric acid, and precipitation by ammonia. It forms white needles, which are hardly dissolved by any solvent except alcohol acidified by hydrochloric acid. Ether and naphtha when heated dissolve but a very small quantity, which yet on cooling nearly fills the liquid with crystals. It inclines to the character of a base, but a very feeble one. Its formula is $C_{56}N_2H_{24}O_2$. It is, therefore, formed by the coalescence of 4 eqs. hyduret of benzoyle, or 2 eqs. benzoine, in which, namely in $C_{56}H_{24}O_8$, 2 eqs. of nitrogen have been substituted for 6 eq. oxygen. Thus, $C_{56}H_{24}O_8 + N_2H_6 = 6HO + C_{56}N_2H_{24}O_2$. It is worthy of remark, that, if we here assume the smaller equivalent of nitrogen, namely, $Az = \frac{N}{3}$, then benzoinam corresponds to 4 eqs. of hyduret of benzoyle $C_{56}H_{24}O_8$, in which Az_6 are substituted for O_6 , yielding $C_{56}H_{24} \left\{ \begin{matrix} O_2 \\ Az_6 \end{matrix} \right\}$.

Hydrocyanate of Benzoine.—Discovered by Zinin. To procure this compound, a mixture of 4 parts of oil of bitter almonds and 1 part of anhydrous prussic acid is added to 1 part of a solution of caustic potash of sp. gr. 1.25, diluted with 6 times its bulk of alcohol. The whole should be gently heated, and laid aside for twenty-four

hours, after which, fine white flocculent crystals form, which may be purified by crystallization from alcohol. It is difficultly soluble in alcohol and ether; in sulphuric acid it dissolves with a green colour; in muriatic acid, potash-ley, and water, it is insoluble. Its formula is $C_{46}H_{18}N_2O_4$; hence it is formed of 3 atoms of hyduret of benzoyle, and 2 atoms of prussic acid, *minus* 2 atoms of water. Gregory has obtained this compound by the action of aqua potassæ on the crude oil, and has, by his analysis, confirmed the above formula. The name, however, cannot be considered as appropriate.

Benzile.—Syn. Benzoyle of Laurent, who first obtained it. To prepare it, chlorine gas is passed over melted benzoine as long as hydrochloric acid escapes. The crystalline mass which remains after cooling is dissolved in hot alcohol, which on cooling deposits crystals of pure benzile. It is sometimes found along with benzoine in the residue of the distillation of raw oil of bitter almonds with hydrate of lime and protochloride of iron, and may easily be separated from that substance by crystallization. But the most simple method of procuring it is, to add 2 parts of pure nitric acid to 1 part of benzoine, and to expose this mixture to a gentle heat; violent action ensues from the escape of nitrous acid, and the benzile appears as a colourless oil on the surface of the liquid. (Zinin.)

Benzile forms large sulphur-yellow, translucent, regular six-sided prisms, belonging to the rhomboidal system; tasteless, inodorous; melting at about 200° ; insoluble in water, soluble in alcohol and ether; of the hardness of sugar, crackling between the teeth; volatile without decomposition; inflammable, burning with a red smoky flame; soluble in oil of vitriol, from which it is precipitated by water; insoluble in an aqueous solution of potash, with which it may be boiled without decomposition; but soluble with decomposition in an alcoholic solution of potash, to which it gives a violet-blue colour, while it passes into benzoic acid.

The empirical formula of benzile is $C_{14}H_5O_2$. It has therefore the composition of the hypothetical radical benzoyle. But it does not exhibit the characters of such a compound, and there is reason to believe that it contains at least 28 eqs. of carbon, in which case its true formula is $C_{28}H_{10}O_4$. Laurent derives this from stilbene, $C_{28}H_{12}$. He supposes 2 eq. hydrogen in the stilbene to be replaced by 2 eqs. oxygen, giving rise to the compound $C_{28}\left\{\begin{smallmatrix} H_{10} \\ O_2 \end{smallmatrix}\right\}$, which he calls stilbène; and this body he supposes to form an oxide or suboxide, $C_{28}\left\{\begin{smallmatrix} H_{10} \\ O_2 \end{smallmatrix}\right\} + O_2$, which is benzile, or suboxide of stilbène.

Hydrocyanate of Benzile.—Discovered by Zinin. When a hot solution of benzile in alcohol is mixed with an equal bulk of anhydrous prussic acid, large rhombic colourless crystals of this substance are formed. They are insoluble in water and muriatic acid, and decomposed by ammonia and nitric acid into benzile and prussic acid. Its formula is $C_{28}H_{10}O_4 + 2CyH = C_{32}H_{12}N_2O_4$; hence it consists of 2 atoms of benzile, and 2 atoms of prussic acid.

Benzilic Acid.—Discovered by Liebig. Obtained by boiling benzoine or benzile with a concentrated alcoholic solution of potash, in which it dissolves easily with a violet-blue colour, which disappears by continued boiling. The alkaline solution is added as long as it causes any blue colour after the previous portion has been decolorized by boiling, and the solution is then carefully neutralized by hydrochloric acid, by which means a resinous matter is separated. To the filtered solution is added an excess of hydrochloric acid, and on cooling the benzilic acid crystallizes.

Benzilic acid forms colourless, transparent, brilliant, rhombic crystals, soluble in cold water sparingly, in hot more easily; fusible at 230° ; not volatile. When strongly heated, it yields benzoic acid which sublimes, a violet-coloured vapour, and a residue of carbon. If brought in contact with cold oil of vitriol, a lively carmine-red colour is developed.

If to the elements of 2 at. benzile those of 2 at. water be added, we have the composition of benzilic acid; in which, however, 1 at. of water is basic, as it can be replaced by metallic oxides.

Its formula, therefore, is $C_{28}H_{11}O_5 + HO$.

The quantity of the resinous matter above mentioned formed with it is always trifling, and most probably is not essentially connected with it. The oxygen of the atmosphere seems to have some share in the production of benzilic acid from benzoine; but these reactions have not yet been sufficiently investigated.

Of the salts of benzilic acid, the potash salt and silver salt have been examined; the potash salt crystallizes in large transparent tables, the silver salt is $C_{28}H_{11}O_5, AgO$, and forms a white crystalline powder insoluble in water. Laurent considers this acid also to belong to the *stillbene* series, and calls it stillbic acid $C_{28}H_{12}O_6$.

Azobenzoilide.—Oil of bitter almonds, prepared by distillation per descensum with steam, gave, when put in contact with ammonia, a brown viscid mass, which, when deprived by means of alcohol and ether of everything soluble in those menstrua, left a residue of azobenzoilide, in the form of a white powder, decomposable by heat.

Formula, $C_{28}H_{11}Az_3 = C_{28} \left\{ \begin{smallmatrix} H_{11} \\ Az \end{smallmatrix} \right\} Az_2$, according to Laurent, who now views it as an azotide of azostilbase.

Picryle.—Discovered by Laurent. When oil of bitter almonds is acted on by sulphuret of ammonium, several new compounds are formed; and when the mass is distilled, it yields, first water, then ammonia, sulphuretted hydrogen, and a variety of oily products. These are followed by a mixture of crystalline compounds, which are separated by means of their greater or less solubility in ether. The most soluble of all is *picryle*, which, when purified, forms colourless octohedrons, insoluble in water. Its formula is $C_{42}H_{15}NO_4$, and it is consequently derived from the coalescence of 3 eqs. of hyduret of benzoyle, which have been partly deoxidized by the sulphuret, and have taken up 1 eq. of nitrogen. This is a good instance of the power of reducing agents to cause the coalescence of atoms so as to yield compounds of high atomic weight—a power very active in the vegetable organism, where from the highly oxidized bodies, carbonic acid and water, with the aid of ammonia, and of great reducing energy, the compounds found in vegetables, and those which serve as food to animals, all distinguished by high atomic weights, are produced. We shall see other proofs of the same mode of action of chemical forces in the bodies accompanying picryle.

Picryle has the composition of an organic base, but its properties are but little known. By the action of nitric acid on picryle, Laurent obtained a yellow crystalline powder, nitripicryle, in which 3 eqs. of hydrogen are replaced by 3 eqs. of nitrous acid. Its formula is $C_{42}H_{12}N_4O_{16} = C_{42} \left\{ \begin{smallmatrix} H_{12} \\ 3NO_4 \end{smallmatrix} \right\} NO_4$.

Along with picryle there are formed lophine, which has been already described, stilbène, and a sulphurised compound, called by Laurent thionessale or sulphessale. As these bodies are best obtained by the distillation of the hyduret of sulphobenzoyle, we shall first describe that compound.

Hyduret of Sulphobenzoyle.—*Syn. Sulphuret of Benzène*.—Formula $C_{14}H_5S_2H$, or $C_{14}H_6S_2$. One vol. of crude essence of bitter almonds is dissolved in 8 or 10 of alcohol, and gradually mixed with 1 vol. of hydrosulphuret of ammonia. After a time the mixture deposits a fine white powder, formed of grains smaller than those of starch, which give to the fingers a very persistent odour of garlic. It is insoluble in water and alcohol. Ether liquefies it, but a few drops of alcohol restore its solid form. It may be considered as the hyduret of a new radical, in which the oxygen of benzoyle has been re-

placed by sulphur. When heated, it melts, and if now allowed to cool, forms first a transparent plastic mass, and afterwards a brittle glass. If kept melted for some time, it crystallizes, but is now altered.

Two views may be taken of the constitution of this compound, as expressed by the formulæ above given. In either case it is hyduret of benzoyle (oxide of benzène, Laurent), in which the oxygen is replaced by sulphur, equivalent for equivalent.

Stilbène.—When the preceding compound is distilled, it yields at first sulphuretted hydrogen and a small portion of a body supposed to be sulphuret of carbon. The residue in the retort does not now distil until a much higher temperature is employed. It consists of two compounds, the more volatile of which, stilbène, distils first, while the less volatile, the sulphessale, comes over last of all. The stilbène is purified by solution in hot alcohol, and when subsequently dissolved in hot ether, the solution yields by evaporation very fine colourless crystals, of a brilliant pearly lustre, resembling that of the mineral stilbite; hence the name. It melts about 230° , and distils at 568° .

By the action of fuming sulphuric acid, it yields a coupled acid, sulphostilbic acid, which forms a soluble salt with baryta. Chlorine, bromine, and nitric acid decompose stilbène, yielding new products. By chromic acid it is again transformed into hyduret of benzoyle.

The empirical formula of stilbène is C_7H_3 ; but its compounds indicate that its true formula is $C_{28}H_{12}$. Here, then, under the reducing influence of sulphuret of ammonium, aided by heat, while the oxygen of hyduret of benzoyle has been removed, 2 eqs. of the hydrate have coalesced to give rise to 1 eq. of stilbène.

When chlorine is passed through melted stilbène, it is absorbed, and gives rise to several new compounds:—1. *Chloride of Stilbène, modification a*.—2. *Chloride of Stilbène, modification b*.

Both of these are crystallizable, and they have both the formula $C_{28}H_{12}Cl_2$. They are both decomposed by being boiled with an alcoholic solution of potash, and each yields an oily liquid of the formula $C_{28}\left\{\begin{smallmatrix} H_{11} \\ Cl \end{smallmatrix}\right\}$. These two liquids Laurent calls *chlostilbase a*, and *chlostilbase b*. They are different; for bromine acts on both, producing with each a compound, *bromide of chlostilbase a*, or *bromide of chlostilbase b*, which are both crystallizable, but in totally different forms.—3. *Chloride of chlostilbase* $C_{28}\left\{\begin{smallmatrix} H_{11} \\ Cl \end{smallmatrix}\right\}Cl_2$, a crystallizable solid.

In these compounds we see an example of what was stated concern-

ing types and substitutions at p. 684. In the two chlorides of stilbène, the two forms of chlostilbase, and the two bromides of chlostilbase, the formulæ and equivalents in each pair are the same, and therefore the differences must depend on the grouping of the atoms. In the two forms of chlostilbase, for example, it is not the same eq. of hydrogen which is replaced by chlorine. We shall see many other illustrations of this important principle.

Bromine acts on stilbène, and produces bromide of stilbène, $C_{28}H_{12}Br_2$, in the form of a white powder.

When stilbène is boiled with nitric acid, it yields three new compounds, namely:—

1. Nitrostilbase $C_{28} \left\{ \begin{smallmatrix} H_{11} \\ NO_4 \end{smallmatrix} \right\}$.
2. Nitrostilbène $C_{28} \left\{ \begin{smallmatrix} H_{10} \\ 2NO_4 \end{smallmatrix} \right\}$; and
3. Nitrostilbic Acid $C_{28} \left\{ \begin{smallmatrix} H_9 \\ NO_4 \end{smallmatrix} \right\} O_8 + 2HO$.

The two former are resinous-looking yellow bodies, the latter is a light, yellow, crystalline powder. In the two former 1 and 2 eqs. of hydrogen are replaced by 1 and 2 eqs. of nitrous acid; while in the third, 2 eq. of hydrogen are removed without replacement, or, at least, assume the form of basic water; while 1 eq. is replaced by nitrous acid, and 8 eqs. of oxygen are added.

Sulphessale.—*Syn. Thionessale.*—This body distils after the stilbène. It is purified by solution in ether; but its best solvent is naphtha. It is a colourless crystallizable solid, fusible at 352° ; but if a crystal of the substance be thrown into the fused mass, it crystallizes even at 450° . It resists the action even of a boiling alcoholic solution of potash, but it is decomposed by potassium. Its empirical formula is $C_{26}H_9S$, and its production, along with stilbène, from the hyduret of sulphobenzoyl, is thus explained, $4(C_{14}H_6S_2) = C_{28}H_{12} + C_{26}H_9S + 2CS_2 + 3HS$. Laurent, however, considers its true formula to be twice as high, namely, $C_{52}H_{18}S_2$.

By the action of bromine it yields bromethionessile $C_{52} \left\{ \begin{smallmatrix} H_{14} \\ Br_4 \end{smallmatrix} \right\} S_2$; and by the action of nitric acid it gives the body called nitrethionessile $C_{52} \left\{ \begin{smallmatrix} H_{14} \\ 4NO_4 \end{smallmatrix} \right\} S_2$.

It may be mentioned in this place that Laurent refers to the stilbène series not only the substances just described, but many of those previously mentioned. The following table contains his views, and it includes several compounds of which I can find no distinct account.

In the table, Az, where it appears, stands for $\frac{N}{3}$, the secondary equivalent of nitrogen admitted in some cases by Laurent.

Stilbène	$C_{28}H_{12}$
Chlostilbase, <i>a</i>	$C_{28} \left\{ \begin{array}{c} H_{11} \\ Cl \end{array} \right\}$
Chlostilbase, <i>b</i>	$C_{28} \left\{ \begin{array}{c} H_{11} \\ Cl \end{array} \right\}$
Chloride of Stilbène, <i>a</i>	$C_{28}H_{12}Cl_2$
Chloride of Stilbène, <i>b</i>	$C_{28}H_{12}Cl_2$
Chloride of Chlostilbase	$C_{28} \left\{ \begin{array}{c} H_{11} \\ Cl \end{array} \right\} Cl_2$
Bromide of Chlostilbase	$C_{28} \left\{ \begin{array}{c} H_{11} \\ Cl \end{array} \right\} Br_2$
Nitrostilbase	$C_{28} \left\{ \begin{array}{c} H_{11} \\ NO_4 \end{array} \right\}$
Nitrostilbène	$C_{28} \left\{ \begin{array}{c} H_{10} \\ 2NO_4 \end{array} \right\}$
Oxide of Stilbène (Benzoine)	$C_{28}H_{12}O_4$
Azotide of Stilbène (Benzoinamide)	$C_{28}H_{12}Az_4$
Stilbous Acid (Benzoate of Hyduret of Benzoyle)	$C_{28}H_{12}O_5$
Stilbite of Potash	$C_{28} \left\{ \begin{array}{c} H_{11} \\ K \end{array} \right\} O_5$
Stilbesious Acid }	$C_{28} \left\{ \begin{array}{c} H_{10} \\ O_2 \end{array} \right\} O_5$
Hyperoxide of Stilbène }	
Azotide of Azostilbase (Azobenzoilide)	$C_{28} \left\{ \begin{array}{c} H_{11} \\ Az \end{array} \right\} Az_2$
Suboxide of Stilbène (Benzile)	$C_{28} \left\{ \begin{array}{c} H_{10} \\ O_2 \end{array} \right\} O_2$
Subazotide of Azostilbène (Azobenzoyle)	$C_{28} \left\{ \begin{array}{c} H_{10} \\ Az_2 \end{array} \right\} Az_2$
Stilbous Acid* (Hypobenzoilous Acid)	$C_{28}H_{12}O_5$
Stilbites	$C_{28} \left\{ \begin{array}{c} H_{10} \\ M_2 \end{array} \right\} O_5$
Stilbic Acid (Benzilic Acid)	$C_{28}H_{12}O_6$
Stilbates	$C_{28} \left\{ \begin{array}{c} H_{11} \\ M \end{array} \right\} O_6$
Nitrostilbic Acid	$C_{28} \left\{ \begin{array}{c} H_{11} \\ NO_4 \end{array} \right\} O_{10}$
Nitrostilbates	$C_{28} \left\{ \begin{array}{c} H_9 \\ NO_4 \\ M_2 \end{array} \right\} O_{10}$
Chlostilbasic Acid (Chlorobenzoic Acid)	$C_{28} \left\{ \begin{array}{c} H_{11} \\ Cl \end{array} \right\} O_{10}$
Salts of that Acid	$C_{28} \left\{ \begin{array}{c} H_9 \\ Cl \\ M_2 \end{array} \right\} O_{10}$
Bromobenzoic Acid	$C_{28} \left\{ \begin{array}{c} H_{11} \\ Br \end{array} \right\} O_{10}$
Bromobenzoates	$C_{28} \left\{ \begin{array}{c} H_9 \\ Br \\ M_2 \end{array} \right\} O_{10}$

The preceding pages contain a very brief and imperfect sketch of the derivatives of benzoyle, or rather of the oil of bitter almonds. It

* This would appear to be a repetition of a former item, the second name being changed. In the former case it is benzoate of hyduret of benzoyle. The table is taken from a summary by Hoffmann.

unfortunately happens that the numerous and interesting papers by Laurent, to whom we are indebted for a very great part of our knowledge on the subject, have appeared at different times in different journals, and have never been published in a connected form by their author, while the frequent changes of nomenclature and of views which necessarily accompany the rapid progress of chemistry, have rendered it a very difficult task to follow out and trace the progress of discovery in this department. Indeed, no systematic work has yet contained anything like a full digest of the researches which have been made on the oil of bitter almonds; and the above most imperfect account can only serve to show how much such a digest is wanted. It is to be hoped that Laurent himself will supply this desideratum.

We see, however, from the facts here recorded, that, under a variety of different circumstances, the molecules of the hyduret of benzoyle may coalesce, yielding compounds in which 2, 3, or more are united to form 1 molecule of the new compound. Thus, the hyduret (C_{14}) may be converted into benzoine (C_{28}); benzoine, acted on by ammonia, yields either benzoinam (C_{56}), or benzoinamide (C_{42}).

Again, the hyduret of benzoyle may yield the hyduret of sulphobenzoyle (C_{14}) from which, by heat, are obtained stilbene (C_{28}), and sulphessale (C_{52}).

Or, again, the hyduret may yield hydrobenzamide (C_{14}), benzhydramide, and amarine (C_{42}), and, as Laurent states, azosulphuret of benzène, a body of which we can find no account, but which is said to contain 126 eq. of carbon, and must, therefore, be formed by the coalescence of 6 eq. of hyduret. Its formula, according to Laurent, is $C_{126}H_{54}S_{12}N_2$.

Not only do the molecules of the hyduret, under the influence of reducing agents, coalesce to form these compounds, but the latter are in almost every case easily resolved, especially when oxidized, into others of lower atomic weights. There can, therefore, be no doubt that the study of these changes will shed great light on the nature of the processes which go on in the living vegetable, and will probably, also, enable us to form artificially many useful compounds hitherto known only as natural productions.

COMPOUNDS RELATED TO THE SERIES OF BENZOYLE.

AMYGDALINE.

Discovered by Robiquet and Boutron Charlard. An ingredient of bitter almonds and of the berries (and leaves?) of the cherry-

laurel (*Prunus Lauro-cerasus*). In order to obtain it, bitter almonds are finely powdered, and strongly pressed between warm iron plates to remove the fixed oil. The residue is repeatedly boiled with alcohol of 93—94 per cent. The decoctions are united, distilled in the water-bath till the alcohol is driven off, and the syrupy liquid which is left diluted with water, a little ferment is added, and the whole is left to itself in a warm situation. Fermentation soon commences, and, after it has ceased, the liquid is filtered, evaporated in the water-bath to the consistence of syrup, and mixed with alcohol of 94 per cent. The amygdaline is almost entirely precipitated in the form of a white crystalline powder. This is squeezed out, and purified by new solutions and crystallizations in alcohol. Amygdaline exists ready formed in the bitter almonds, and is dissolved by the alcohol along with sugar. The latter substance impedes the crystallization of the amygdaline; and this impediment is removed by the fermentation. About 3 or 4 per cent. of amygdaline are obtained.

Amygdaline crystallizes out of alcohol in silky scales or short needles, which have no smell, but a faint taste of bitter almonds. At a high temperature it is decomposed with an odour of hawthorn blossoms, and leaves a voluminous coal. It is hardly soluble in cold alcohol, but somewhat soluble at the boiling temperature. The crystals contain alcohol, which they lose on exposure to the air. It is very soluble in water. A solution saturated at 104° gives on cooling large silky transparent prisms, containing 6 at. (10·57 per cent.) of water; of which they lose, when placed under a jar near oil of vitriol, 2 at. (3·52 per cent.) In dry chlorine it undergoes no change: in moist chlorine it is decomposed, swelling up, and leaving a white powder, soluble in water and in alcohol, not yet examined. When acted on by dilute nitric acid, or by hyperoxide of manganese and sulphuric acid, it is resolved into ammonia, hyduret of benzoyle, benzoic acid, formic acid, and carbonic acid, the latter passing away as vapour and gas during the distillation. With caustic alkalies it is resolved into amygdalinic acid and ammonia; with hypermanganate of potash it is resolved into cyanate and benzoate of potash.

Formula, $C_{40}H_{27}O_{11}N$.

AMYGDALINIC ACID.

Discovered by Wöhler and Liebig. Obtained by dissolving amygdaline in barytic water, and boiling the solution as long as ammonia is evolved. The baryta is then precipitated by sulphuric acid, and the filtered liquid evaporated in the water-bath. It forms a colourless,

transparent, amorphous mass, having a pleasant acid taste, which deliquesces in moist air, and is insoluble in alcohol and ether. When heated with nitric acid, or with hyperoxide of manganese and sulphuric acid, it produces hyduret of benzoyle, with formic and carbonic acids. It forms with all bases salts soluble in water, and with oxide of lead a basic salt which is insoluble. These salts are little known. The formula of amygdalinic acid is $C_{40}H_{26}O_{12} + aq.$ In the anhydrous amygdalate of baryta, the atom of basic water in the above formula is replaced by an atom of baryta.

APPENDIX TO THE COMPOUNDS OF BENZOYLE.

Aqueous solution of hyduret of benzoyle, containing also hydrocyanic acid, or distilled water of bitter almonds.

Prep.—Two pounds of powdered bitter almonds, freed from all fixed oil by pressure between heated iron plates, are made with cold water into a thin paste in a stoppered vessel. After macerating for twelve hours it is distilled; and in order to avoid burning the mass, this is best done by means of steam, or in a bath of chloride of calcium. Two pounds of liquid are distilled off.

It is a somewhat milky liquid, having a strong smell and taste both of hydrocyanic acid and of oil of bitter almonds. It generally deposits, when allowed to rest, a certain quantity of oil (hyduret of benzoyle, containing hydrocyanic acid). After 24 hours the water becomes clear; and frequently becomes again turbid in bottles containing air. Freshly prepared, it contains in 1 ounce $1\frac{1}{4}$ grain of anhydrous hydrocyanic acid (equal to about 33 drops of the ordinary medicinal acid of this country, containing 3·2 per cent. of anhydrous acid), but its strength in this respect diminishes very much by long keeping. This water possesses this peculiarity, that the hydrocyanic acid contained in it cannot be at once precipitated as cyanide of silver by the addition of nitrate of silver. This precipitation takes place, however, perfectly, if nitrate of silver and ammonia be both added to the water, and the ammonia neutralized after a time by nitric acid, when the cyanide of silver separates. A solution of pure hyduret of benzoyle, to which hydrocyanic acid has been added, acts exactly in the same way. The distilled water of bitter almonds, mixed with hydrochloric acid, and evaporated, yields a residue of formobenzoic acid and sal-ammoniac. It is used in medicine, and is poisonous.

LAUREL WATER.

Two parts of the fresh leaves of *Prunus Lauro-cerasus* L. are distilled with water till 3 parts have passed over. This water resembles the preceding, and is used for the same purposes.

Most pharmacopœias recommend an addition of spirit of wine to these distilled waters. Before the distillation this is useless, and even hurtful. Afterwards it prevents turbidity, but gives the water a tendency to become acid.

ON THE FORMATION OF HYDURET OF BENZOYLE FROM BITTER ALMONDS.

The white part both of sweet and bitter almonds consists chiefly of a substance which is very remarkable on account of a peculiar decomposition which it suffers in contact with amygdaline and water, and produces also in the amygdaline. Wöhler and Liebig named this substance Emulsine. Robiquet has obtained it in a separate form, and calls it Synaptase. It is soluble in water, and is precipitated by alcohol in white flocks, which may be again dissolved in water. It is precipitated neither by acids nor by acetate of lead. At 140° it coagulates like albumen; it contains nitrogen, and when boiled with alkalis is resolved into ammonia and a new acid. If 10 parts of amygdaline be dissolved in 100 of water, and mixed with an emulsion of sweet almonds, or with a solution of 1 part of synaptase in 10 of water, the reaction above alluded to instantly commences; the liquid, without losing its transparency, becomes slightly opalescent by reflected light; the smell of bitter almonds is perceived in the solution; and when distilled, both hydrocyanic acid and hyduret of benzoyle pass over with the vapour of water. The residue in the retort is turbid from coagulated synaptase; and if evaporated yields a very sweet syrup, which contains crystallizable sugar, and a fixed acid, which is perceived after the sugar has been destroyed by fermentation. The quantity of sugar is greater than could be formed out of the elements of the quantity of amygdaline originally present, so that the elements of the synaptase appear to be essentially concerned in its production.

The complete decomposition depends on the quantity of the water in which the amygdaline and synaptase are dissolved; if there be less than is required to dissolve the hyduret of benzoyle produced, a proportionate quantity of amygdaline remains undecomposed. Coagulated synaptase has no appreciable action on amygdaline.

These facts serve to explain a series of phenomena which have long been known. In bitter almonds amygdaline and synaptase, along with fixed oil, are present, but in such a form that the two former cannot act on each other. The drying of the almonds, by removing all water, also prevents this reaction. By squeezing the bruised almonds, the fixed oil is separated; and the marc, if boiled with alcohol, yields to that solvent the amygdaline, while the synaptase is coagulated.

When the marc is moistened with cold water, the reaction above described instantly commences. The smell and taste of hydrocyanic acid and hyduret of benzoyle are perceived. If the emulsion be made with little water, a corresponding quantity of amygdaline remains undecomposed, and may be obtained in crystals by means of alcohol. But if there be a sufficient quantity of water, all traces of amygdaline disappear after a time.

If the newly pressed marc be thrown into boiling water, the synaptase is brought by the heat into that state in which it ceases to act on the amygdaline; and if the marc be now distilled with water, neither hydrocyanic acid nor hyduret of benzoyle is formed at all.

When we wish, therefore, to obtain the oil, or the distilled water, for medical use, we must, for the above reasons, make the pressed marc into a paste with about 20 parts of luke-warm water, and leave the mixture to itself for 24 hours.

One hundred parts of amygdaline yield 47 of raw oil, containing 5.9 of anhydrous hydrocyanic acid. Hence 17 grains of amygdaline, dissolved in a fluid ounce of an emulsion of sweet almonds, yield a liquid containing one grain of anhydrous acid, which does not require to be distilled. This mixture has been proposed as a uniform preparation, to replace the very variable distilled water, by Wöhler and Liebig. The great tendency both of hydrocyanic acid and hyduret of benzoyle to be changed when in contact with air and water into many new compounds, is the cause of the loss of strength which the distilled water undergoes when long kept. But amygdaline keeps perfectly in the solid form; and when the above mixture is made only in small quantities, as it is prescribed, it will be found perfectly uniform in strength, as it need not be kept long.

The leaves of the cherry-laurel seem in like manner to contain amygdaline, along with some substance which, like synaptase, has the power of decomposing it; for the laurel water contains the same ingredients as the distilled water of bitter almonds.

Amygdaline contains in 1 atom the elements of 1 eq. hydrocyanic acid, 2 eq. hyduret of benzoyle, 1 at. sugar ($C_6H_5O_5$), 2 eq. formic acid, and 7 at. water. Amygdalinic acid contains the elements of 2 eq.

hyduret of benzoyle, 1 of sugar, of 3 eq. formic acid, and 6 of water. Robiquet (*Journ. de Pharm.* 1838, p. 328) has made known a process by which we may obtain synaptase, the peculiar substance above mentioned, which possesses the property of decomposing amygdaline in contact with water. It is as follows:—Sweet almonds, freed by pressure as completely as possible from fixed oil, are mixed with twice their weight of water, and after macerating for two hours, exposed to pressure in a cloth. The squeezed liquid is filtered, and acetic acid added as long as it causes a thick white precipitate of vegetable albumen. Acetate of lead is then added to separate gum; and a liquid is thus obtained, which contains only free acetic acid, acetate of lead, sugar, and synaptase. The oxide of lead is removed by sulphuretted hydrogen, and the synaptase is then thrown down by the addition of alcohol. The sugar and free acetic acid remain dissolved. The precipitate is washed with alcohol, and dried in vacuo over sulphuric acid.

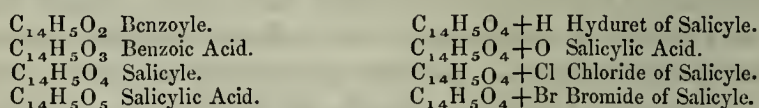
When dry, it forms a yellowish-white, hard, brittle, opaque, horny mass, very soluble in cold water. The solution speedily undergoes spontaneous decomposition, becomes muddy, and acquires a putrid odour. Tincture of iodine produces in the fresh solution an intense rose-red colour, without causing a precipitate. The composition of synaptase is not yet ascertained.

When an emulsion of sweet almonds is deprived of all fixed oil by means of ether, a clear viscid liquor is obtained, which, when mixed with alcohol, gives a thick white precipitate, drying into a semi-transparent horny mass. This is the substance which was called emulsine by Wöhler and Liebig; but which, as would appear from Robiquet's process above described, contains vegetable albumen mixed with synaptase. Richardson and Thomson jun. have analysed this emulsine, but their results need not be quoted here, as the substance is admitted to have been a mixture. They found that, when boiled with baryta or caustic alkalies, it yielded abundance of ammonia.

SALICYLE.

Under the name of hyduret of salicyle, a peculiar acid was made known by Piria, who discovered it as a product of the decomposition of salicine. The interest excited by its uncommon properties was increased in an unwonted degree by some researches of Dumas, which rendered it very probable that this substance was identical with one of the ingredients of an essential oil, first obtained by Pagenstecher by distilling the flowers of *Spiræa ulmaria* (meadowsweet), and described by

Löwig as hyduret of spiroyle. Ettling, by very exact analyses, put beyond all doubt the identity of these two substances. According to Ettling and Piria, the composition, both of the oil produced by the decomposition of salicine, and of the oil of *Spiræa ulmaria*, is the same as that of crystallized benzoic acid. This oil, which is an acid, combines with bases to form salts which have the same composition as the benzoates; but the difference in their properties is so great, that they cannot be confounded together. From the reactions of this acid with chlorine and with caustic alkalies, Dumas drew the conclusion, that it contains a radical, which may be regarded as a higher degree of oxidation of benzoyle. With hydrogen this radical forms hyduret of salicyle; with oxygen, salicylic acid. In contact with chlorine, bromine, and iodine, the hydrogen of the hyduret is replaced by an equivalent of these elementary bodies; a reaction which he compares to the formation of chloride of benzoyle from the hyduret of benzoyle. The following formulæ represent these views:—



If we merely look at the composition of these compounds, this view of them appears extremely probable. Indeed it was originally proposed by Löwig for the oil of spiræa, some years before it was possible to suspect the identity of two substances obtained from sources so different; although his analytical results, in regard to the actual composition of that body, were not confirmed by subsequent researches. The late investigations into the constitution of many salts of organic acids have shewn that many, perhaps all, of these acids must be regarded as hydrogen acids; and in this case the great analogy with hyduret of benzoyle renders it advisable to adopt that view which regards the oil of spiræa as hyduret of salicyle, bearing in mind, however, that it may also be viewed as a hydrated oxygen acid, isomeric or polymeric with benzoic acid.

The hypothetical radical salicyle is unknown in a separate form. Its formula, as above mentioned, is $C_{14}H_5O_4$, differing from benzoyle by containing 2 eq. of oxygen more. It is represented by the symbol Sa.

HYDURET OF SALICYLE.

Syn. Salicylous acid. Hyduret of Spiroyle.—Discovered by Pagenstecher in the volatile oil of *Spiræa ulmaria*; by Piria as a product of the decomposition of salicine. The latter ascertained its nature

and composition. The identity of the two was rendered probable by Dumas, and proved by Ettling's analysis of the oil of spiræa.

To obtain it, the oil of spiræa is distilled with aqua potassæ in excess as long as neutral oil passes over. The residue, a solution of a compound of the hyduret with potash, is supersaturated with dilute sulphuric acid, and again distilled, when the acid hyduret distils over with the vapour of water. Or according to Piria: a mixture of 1 part of salicine, 1 part bichromate of potash, $2\frac{1}{2}$ of oil of vitriol, and 20 of water, is subjected to distillation. The salicine is dissolved in part of the water, the acid is diluted with the rest; the whole materials are then mixed in a retort, when heat is developed, and a gentle effervescence appears. When this is over, the distillation is commenced: $\frac{1}{2}$ lb. salicine gives about 2 oz. of hyduret of salicyle. (Ettling.) In both processes the distilled liquid contains the hyduret, which separates from the water. It is purified by washing with water and rectification along with chloride of calcium.

Formula, $C_{14}H_5O_4 + H = SaH$.

It is a colourless or pale yellow, oily, inflammable liquid; sp. gr. 1.1731; boiling at 370° , or, according to Piria, at 380° ; becoming solid at -4° . (Löwig.) It has a burning taste and a pleasant aromatic odour; is somewhat soluble in water, and mixes with alcohol and ether in all proportions. Its solution reddens litmus first, then bleaches it. Concentrated sulphuric acid decomposes it. When placed in contact with chlorine or bromine, 1 eq. hydrogen is removed, which forms hydrochloric or hydrobromic acids; and its place supplied by 1 eq. chlorine or bromine, producing chlorosalicylic and bromosalicylic acids. Hyduret of salicyle, heated with excess of hydrate of potash, gives out hydrogen gas, while salicylic acid is formed. With potassium, hydrogen is also disengaged, being replaced by the metal.

Hyduret of salicyle has distinct acid properties, and when in contact with bases, neutralizes them, forming salts, while water is separated. Viewed as a hydrogen acid, the reaction is very simple, for with a metallic oxide, MO , we have $SaH + MO = SaM + HO$; and accordingly SaM is the general formula of these salts, which may be called salicylurets.

But the hyduret of salicyle may also be viewed as a hydrated oxygen acid, $C_{14}H_5O_3 + HO$, isomeric with benzoic acid; and in that case the reaction with a base will be, on the hydratic theory of acids, $C_{14}H_5O_3HO + MO = C_{14}H_5O_3MO + HO$. On this view, the hyduret of salicyle is called salicylous acid, and its salts salicylites. But it must be remembered, that, on the hydrogen theory of acids, benzoic acid itself is represented as a hydrogen acid.

HYDURET OF SALICYLE WITH BASES.

Salicyluret of Ammonium.—Prepared by adding strong aqua ammonia to hyduret of salicyle. A yellow solid mass, without taste, having a faint odour of roses; sparingly soluble with a yellow colour in cold water and alcohol, more readily dissolved by hot alcohol. By the cooling of a saturated solution transparent needles of a pale yellow are obtained. It is spontaneously decomposed if kept moist; becomes black, semi-fluid, and exhales ammonia with a penetrating smell of roses. (Löwig.) Dry hyduret of salicyle easily absorbs dry ammonia; and the compound, according to Ettling, contains 3 atoms of the acid and 2 atoms of ammonia.

Salicylimide.—If hyduret of salicyle be dissolved in three times its volume of alcohol, and ammonia added drop by drop, the liquid concretes into a solid paste of fine yellow needles. With the aid of a moderate heat these crystals dissolve; and the solution, if left to rest, deposits golden-yellow, brilliant, transparent prisms, which when dry are hard and pulverizable. Here 3 at. of the acid are acted on by 2 of ammonia, 6 at. of water being eliminated. The alcoholic liquid in which these crystals have formed is no longer able, even at a boiling heat, to dissolve them. They now require a threefold quantity of alcohol. This would indicate that at first salicyluret of ammonium is formed, which by a longer contact with ammonia, and a slow separation of the crystals, passes into salicylimide. This body is decomposed by a high temperature. Heated with acids and alkalis, it is resolved into hyduret of salicyle and ammonia. It is insoluble in water.

Formula, $C_{42}H_{18}O_6N_2$. (Ettling.)

Salicyluret of Potassium.—This is best obtained by adding hyduret of salicyle to a warm solution of potash in alcohol, and allowing the whole to cool, when the salt separates almost pure in the form of four-sided pearly tables nearly colourless, very soluble in water, spontaneously decomposed by exposure to the air in a moist state. It contains water of crystallization, which is expelled by a heat of 212° .

Formula, $2(C_{14}H_5O_4) + \left\{ \begin{matrix} K \\ H \end{matrix} \right\}$. The composition of this salt is that of the acid salt of a bibasic hydrogen acid, and it is probable that the hyduret is bibasic, in which case its equivalent and formula will be double those of benzoic acid. When the salt just mentioned is dissolved in alcohol, and hyduret of salicyle added, there are formed crystals of a still more acid salt.

Salicylurets of Sodium, Calcium, Barium, and Magnesium may

be formed directly. They have the properties of the potash salt. The salt of sodium contains 2 at. water of crystallization, expelled by a heat of 230° . There is likewise an acid salt of sodium in fine shining needles. Salicyluret of copper is anhydrous and green. The salts of zinc and mercury are yellow and insoluble.

Salicyluret of Lead; Basic.—Hyduret of salicylure is dissolved in weak alcohol, and acetate of lead added to the boiling solution. On cooling the salt is deposited, and is purified by boiling alcohol from any adhering acid. It is a lemon-yellow powder, which, when heated, froths up, giving off water and acid; insoluble in water. Its formula is $C_{14}H_5O_3 + 2PbO$. If the hyduret be added to diacetate of lead, a yellow powder of the same composition is precipitated.

Salicyluret of Silver.—According to Löwig, oxide of silver dissolves with apparent decomposition in an aqueous solution of hyduret of salicylure; but this is denied by Ettling. A solution of nitrate of silver mixed with one of salicyluret of potassium, causes a greenish-yellow precipitate, which, when heated, is reduced without disengagement of gas, the vessel being silvered by the reduced metal.

When *salicyluret of copper* is distilled, it yields salicylic acid, and a new crystalline compound, which Ettling, who discovered it, has named *parasalicylure*, the formula of which is $C_{14}H_5O_3$, that is, the same as that of anhydrous benzoic acid, or hyduret of salicylure *minus* 1 eq. oxygen. The true equivalent and relations of this compound are not yet ascertained.

Melanic Acid.—Discovered by Piria. When salicyluret of potassium is exposed to the air, it acquires a green colour, which, after some time, becomes black. When no further change is perceived, the hyduret is completely converted into acetic acid and a black powder. The acetic acid thus formed is in the exact proportion to combine with all the potash contained in the original salt. The black powder possesses acid properties, and unites with bases; from which circumstance it has received its name.

The formula of melanic acid is $C_{10}H_4O_5$.

Three equivalents of oxygen and two of water unite with one atom of hyduret of salicylure, and convert it into one equivalent of acetic, and one equivalent of melanic acid.

SALICYLIC ACID.

Discovered by Piria. This acid is prepared by heating hyduret of salicylure with caustic potash. The mixture at first assumes a brown colour, but the heat must be continued until it is entirely white. At

this time hydrogen is disengaged. The residue is to be dissolved in water, and treated with a mineral acid, which separates the salicylic acid. In order to obtain it pure, it must be repeatedly crystallized. Salicylic acid is likewise formed when coumarine (stearoptene of the Tonka bean) is treated with potash in a similar manner.

Gerhardt has shewn that this acid may also be obtained by heating salicine with fused potash; and, finally, it has been found as a natural product, combined with the oxide of methyle, in the oil of *Gaultheria procumbens*. When this oil is heated with solution of potash, and the solution supersaturated by an acid, the salicylic acid is deposited in large quantity.

Its formation from hyduret of salicyl is very simple. $C_{14}H_5O_4.H + KO.HO = C_{14}H_5O_5.KO + H_2$. The formula of hydrated salicylic acid is $C_{14}H_5O_5.HO$, and it is derived from the hyduret by the addition of 2 eqs. of oxygen, just as benzoic acid is from the hyduret of benzoyl.

Salicylic acid sublimes without decomposition, and may be thus obtained in the form of long crystalline needles, very similar in their appearance to benzoic acid. It crystallizes from water in fine tufts, or long prisms of considerable size. This acid dissolves with difficulty in cold water, but very easily both in hot water and in alcohol. Sulphuric acid decomposes it when they are heated together.

The formula of salicylic acid is $C_{14}H_5O_5 + HO$.

The salts of this acid have been little examined; they are generally crystallizable, and when heated yield carbolic acid (hydrate of phenyle, phenole). The salicylate of ammonia, however, when heated yields salicylamide and water. $C_{14}H_5O_5.NH_4O = C_{14}H_5O_4.NH_2 + 2HO$. The salicylate of silver is insoluble in water, and has the formula $C_{14}H_5O_5 + AgO$. This acid and all its salts possess the property of striking a deep purple colour with the compounds of peroxide of iron, a character which is also found in the hyduret of salicyl.

Nitrosalicylic Acid.—When salicylic acid is acted on by strong nitric acid, without the aid of heat, the first effect is to convert it into a crystallizable acid, which was at first called nitrosalicylic acid, but which has been recognized to be identical with anilic or indigotic acid, an acid formed by the action of nitric acid on indigo. It is salicylic acid, in which 1 eq. hydrogen has been replaced by 1 eq. nitrous acid: $C_{14}\left\{\begin{matrix} H_4 \\ NO_4 \end{matrix}\right\}O_5, HO = C_{14}NH_4O_9, HO$. This acid will be described among the derivatives of indigo.

Nitropicric Acid.—By the further action of nitric acid, aided by heat, salicylic acid is converted into a very bitter acid, called nitro-

picric, carbazotic, or nitrophenic acid, another of the derivatives from indigo, to be afterwards described. The formula of this acid is $C_{12}N_2H_3O_{13},HO$. As it only contains 12 eqs. of carbon, it is evident that 2 eqs. have been separated in the form of carbonic acid, and that a new radical is thus formed. This is confirmed by the action of heat on salicylic acid, whether alone or in contact with bases.

Carbolic Acid.—When salicylic acid is heated along with baryta or lime, or, still better, when it is mixed with glass-powder and heated alone, the action in contact with bases being too violent, it is resolved into carbonic acid, which, when a base is present, combines with it, and a liquid which distils over, and is found to be the compound called by Runge, who discovered it, Carbolic acid, from its occurrence in coal tar, and by Laurent, Hydrate of Phenyle. The formula of this body is $C_{12}H_6O_2$, and it is evident that hydrated salicylic acid, $C_{14}H_6O_6$, is resolved by heat into 2 eqs. carbonic acid $= C_2O_4$ and 1 eq. carbolic acid $= C_{12}H_6O_2$. Carbolic acid, which will be described hereafter as a product of the destructive distillation, has a very strong resemblance to creosote, having the same burning taste, smoky smell, and antiseptic power. It is converted by nitric acid into nitropicric acid; so that it is probable that when salicylic acid is acted on by nitric acid, there is produced some compound of the same series as carbolic and nitropicric acids, which is afterwards oxidized into nitropicric acid. According to Laurent, the carbolic acid series is derived from the body $C_{12}H_6$ (benzine or benzole), which he calls phene, by oxidation and substitutions. They may also be referred, and in some cases with greater probability, to the hypothetical compound $C_{12}H_8$. It is in either case interesting to observe the relation subsisting between salicylic acid, a natural product, and the compounds we have mentioned as derived from the decomposition of indigo, or from the destructive distillation of organic matter, on the one hand, and the hyduret of salicylic acid, salicine, coumarine, and all the compounds which yield salicylic acid, on the other. Indeed, on this side there is even a more direct connexion between salicylic acid and benzoyle than appears from their formulæ; for Ettling has shewn, that, when benzoate of copper is distilled, salicylic acid is one of the products.

CHLOROSALICYLIC ACID.

Syn. Chloride of Salicylic acid, Chloride of Spiroyle. Dry chlorine gas is passed through anhydrous hyduret of salicylic acid as long as hydrochloric acid is disengaged. On cooling, the compound becomes solid and crystalline. It is purified by crystallization out of a hot alcoholic

solution, which deposits it on cooling in the form of pale yellow, oblique, rhombic tables, of a pearly lustre, having a peculiar aromatic odour, fusible and volatile without decomposition. It is inflammable, and burns with a green flame. It is insoluble in water, soluble in alcohol and ether. It combines with alkalies, and is separated from them unchanged by acids. Its solution in alcohol gives with acetate of copper a greenish-yellow, and with acetate of lead a yellow precipitate. Persalts of iron are tinged by it of a dark blue. When heated with potassium, it is decomposed with heat and light. Ammoniacal gas converts it into chlorosalicylimide, analogous to salicylimide.

This compound is distinguished from all analogous compounds of chlorine with compound radicals by its power of combining with bases, and of resisting the action of those bodies. It forms with metallic oxides peculiar salts, in which 1 at. chlorosalicylic acid is combined with 1 at. metallic oxide; so that they may be considered as compounds of salicylic acid in which 1 eq. of oxygen has been replaced by chlorine, $C_{14}H_5 \left\{ \begin{smallmatrix} O_4 \\ Cl \end{smallmatrix} \right\} + MO$.

Formula of the anhydrous chlorosalicylic acid, $C_{14}H_5 \left\{ \begin{smallmatrix} O_4 \\ Cl \end{smallmatrix} \right\}$; of the hydrated acid, $C_{14}H_5 \left\{ \begin{smallmatrix} O_4 \\ Cl \end{smallmatrix} \right\}, HO$.

Chlorosalicylimide.—Formed by the action of ammonia on the preceding compound. Dry ammonia is passed over chlorosalicylic acid in a proper apparatus as long as water is formed. The new substance is left behind in a state of purity. It forms a solid deep yellow mass, insoluble in cold water, decomposed by hot water, acids, and alkalies, with the formation of ammonia and chlorosalicylic acid. Three at. chlorosalicylic acid with 2 eq. ammonia produce 6 at. water and 1 at. chlorosalicylimide, $C_{42}H_{15}O_{12}Cl_3 + N_2H_6 = 6HO + C_{42}H_{15}Cl_3N_2O_6$.

It hence appears to be salicylimide, in which 3 eq. hydrogen are replaced by 3 eq. chlorine.

BROMOSALICYLIC ACID.

This compound, in its preparation, properties, and action with ammonia, is completely analogous to the preceding. Formula, $C_{14}H_5 \left\{ \begin{smallmatrix} O_4 \\ Br \end{smallmatrix} \right\}$.

IODOSALICYLIC ACID.

Hyduret of salicylic acid dissolves iodine in great quantity, without apparent decomposition. But iodosalicylic acid may be obtained by distilling iodide of potassium with chlorosalicylic acid. It sub-

limes in the form of a dark brown fusible mass, analogous in its relations to the two preceding compounds. Formula, $C_{14}H_5\left\{\begin{smallmatrix} O_4 \\ I \end{smallmatrix}\right\}$.

APPENDIX TO SALICYLE.

VOLATILE OIL OF SPIRÆA ULMARIA.

According to the researches of Pagenstecher, this oil is not readily formed in the flowers, but is a product of the action of water during the distillation. The oil, as obtained, is yellow, and is a mixture of two, perhaps three, volatile oily substances, one of which has been described as hyduret of salicyle, or salicylous acid. When the oil has been exposed for some weeks to a cold of from 0° to 4° , large transparent crystals of the hyduret separate, which melt at the ordinary temperature. The oil contains, besides, a substance like camphor, crystallizing in pearly scales, which are solid at the ordinary temperature. If the oil be mixed with aqua potassæ, the hyduret combines with potash, while the neutral oil is separated, and may be obtained by distillation. It is colourless, less volatile than water, and has, like the acid, the smell of the plant. It has not been further examined.

SALICINE.

Discovered by Le Roux and Buchner. It is found in the bark and leaves of all bitter willows: in *Salix helix* W. (*Salix monandra* Hoffm. *Salix purpurea* L.); also in *Salix amygdalina* L. (*Salix triandra*), &c., and in some species of poplar.

Dried or fresh willow bark is cut small, and exhausted by repeated boiling with water. The decoctions are concentrated, and, while boiling, treated with litharge till the liquid appears nearly colourless. The dissolved oxide of lead is removed first by sulphuric acid, afterwards by sulphuret of barium, and, after the separation of the sulphuret of lead, evaporated, when salicine crystallizes, and is purified by repeated solution and crystallization. (Merck.) From willow bark which is fresh and rich in salicine, it may be obtained by cautious evaporation of the cold aqueous infusion. (Merck.) The oxide of lead removes from the solution gum, tannin, and extractive matter, which would impede the crystallization of the salicine. It also combines with the salicine, forming a kind of salt, which is decomposed by the sulphuric acid and sulphuret of barium. If the latter be carefully added, neither sulphuric acid nor baryta remains in the solution; and the sulphuret of lead, which separates, acts as a decolorizing agent.

Salicine crystallizes in white, transparent, inodorous, silky needles and laminae, permanent in the atmosphere. It has a bitter taste, and does not act on vegetable colours. At 212° it loses no weight; it melts at 230° , and is decomposed at a higher temperature, becomes yellow, resinous in appearance, and gives off vapours which burn with a bright flame, leaving a voluminous coal, which when burned leaves no residue. Salicine dissolves in 5.6 parts of water at the ordinary temperature, and to any extent in boiling water. It is soluble in alcohol, but not in ether or fixed oils. It is not precipitated by any reagent. It dissolves in strong sulphuric acid with a blood-red colour, by which character its presence in the willow bark may be recognized. It yields, when acted on by nitric acid, much carbazotic acid. Hydrochloric acid and dilute sulphuric acid change it into a white, tasteless powder, insoluble in water (*saliretine*), soluble in alkalies and alcohol, from which it is again precipitated by acids and water. The liquid in which saliretine has been formed contains grape sugar. (Piria.) Subacetate of lead does not precipitate salicine till ammonia be added, when a white precipitate appears.

Distilled with bichromate of potash and sulphuric acid, salicine yields formic acid, carbonic acid, and hyduret of salicycle. Treated with chlorine, chlorosalicine is produced.

According to the recent researches of Piria, the formula of salicine is $C_{26}H_{18}O_{14}$, and it is composed of sugar $C_{12}H_{10}O_{10}$, and a new body, saligenine, $C_{14}H_8O_4$.

When salicine is warmed to 104° with synaptase, the albuminous principle of the sweet and bitter almond, which we have seen acts as the proper ferment to amygdaline, it is resolved into these two compounds. The saligenine for the most part crystallizes out, and the residue may be obtained by agitating the liquid with ether, in which it is soluble, while the sugar remains dissolved. By heating the solution, the synaptase is coagulated, and the sugar is then obtained by evaporation of the filtered liquid, in the form of grape sugar, $C_{12}H_{14}O_{14}$.

Saligenine.—This substance forms pearly crystals of great beauty, which are very soluble in water, alcohol, and ether. By the action of diluted acids, aided by heat, it is converted into saliretine; and this explains the action of acids in resolving salicine into saliretine and sugar. In this case, however, saligenine is first formed, and then converted into saliretine. The solution of saligenine gives, with aqueous solutions of sesquichloride of iron, or of the salts of sesquioxide of iron, a deep indigo blue colour.

Saligenine is not altered by mere exposure to the air; but if mixed with platinum black, it is oxidized, thereby losing 2 eq. of hydrogen,

and being converted into hyduret of salicyl and water. According to Piria, these are the only products of the oxidation of saligenine, whether in the above way, or by means of chromic acid, bichromate of potash and sulphuric acid, or oxide of silver. This explains the production of the hyduret of salicyl from salicine, formerly described.

Saliretine.—This substance has in some degree the character of a resin. It is formed when salicine or saligenine is heated with dilute acids, and Piria has rendered it probable that it is the only product of the reaction, except water, and that saligenine, *minus* 2 eq. of water, is saliretine. Now, as saligenine is $C_{14}H_8O_4$, if 2 eq. of water be removed, we shall have $C_{14}H_6O_2$ for the formula of saliretine. This is the formula of hyduret of benzoyl and of benzoine.

ACTION OF CHLORINE UPON SALICINE.

When a current of chlorine gas is passed through salicine suspended in 4 parts of water, there is formed in the first instance a crystallizable compound, *chlorosalicine*; and if the action be carried further, two other compounds, also crystallizable, namely, *bichlorosalicine* and *perchlorosalicine*. These three bodies are very analogous to salicine, and are, in fact, salicine, in which 1, 2, and 3 eq. of hydrogen have been replaced by chlorine. It is, however, the hydrogen of the saligenine, and not that of the sugar, which is thus replaced; for in contact with synaptase, these chlorinized compounds are resolved into sugar, and into three compounds analogous to saligenine, namely, chlorosaligenine, bichlorosaligenine, and perchlorosaligenine. Piria, therefore, considers chlorosalicine and the two other corresponding compounds to be like salicine composed of sugar, and in each case a compound playing the part of saligenine.

Chlorosalicine $C_{26}\left\{\begin{smallmatrix} H_{17} \\ Cl \end{smallmatrix}\right\}O_{14}$ is made up of sugar $C_{12}H_{10}O_{10}$ and chlorosaligenine $C_{14}\left\{\begin{smallmatrix} H_7 \\ Cl \end{smallmatrix}\right\}O_4$. Bichlorosalicine $C_{26}\left\{\begin{smallmatrix} H_{16} \\ Cl_2 \end{smallmatrix}\right\}O_{14}$ is formed of sugar and of bichlorosaligenine $C_{14}\left\{\begin{smallmatrix} H_6 \\ Cl_2 \end{smallmatrix}\right\}O_4$; and perchlorosalicine $C_{26}\left\{\begin{smallmatrix} H_{15} \\ Cl_3 \end{smallmatrix}\right\}O_{14}$ is formed of sugar and perchlorosaligenine $C_{14}\left\{\begin{smallmatrix} H_5 \\ Cl_3 \end{smallmatrix}\right\}O_4$.

Piria has also shewn, that, just as salicine and saligenine are converted into a resinous compound, saliretine, by being heated with di-

luted acids, so chlorosalicine and chlorosaligenine, as well as the other more highly chlorinized compounds, are also converted into resinous substances, which bear to saliretine the same relation that chlorosalicine, &c. do to salicine.

These resins will be named chlorosaliretine, bichlorosaliretine, and perchlorosaliretine, and they will be derived from saliretine by the substitution of chlorine for 1, 2, and 3 eq. of hydrogen.

These singular compounds, as described by Piria, are excellent examples of the law of substitution: for we see salicine, saligenine, and saliretine each giving rise to three chlorinized compounds, formed according to that law, and in each group the type remains unchanged.

Thus, salicine, chlorosalicine, bichlorosalicine, and perchlorosalicine are all decomposed by synaptase, yielding sugar and the soluble compounds, saligenine, &c., all of which strike a deep blue with the sesquichloride of iron. Again, saligenine and its congeners, chlorosaligenine, &c., are converted by acids into saliretine and its congeners, chlorosaliretine, &c., which are resinous.

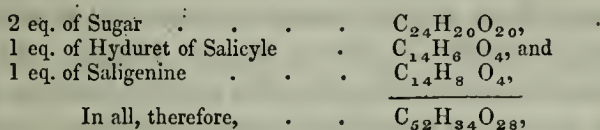
ACTION OF NITRIC ACID ON SALICINE.

When salicine is heated with strong nitric acid it is converted into oxalic and nitropicric acids; but when the acid is less concentrated and the action more moderate, there are formed several substances before the complete conversion into those two. Among these are anilotic acid, an acid very similar to anilic or nitrosalicylic acid, anilic acid, and a neutral body, called by Piria helicine.

Helicine.—When 1 part of salicine is mixed with 10 parts of nitric acid of sp. gr. 1.15, and the mixture left to itself, the salicine slowly dissolves, and soon afterwards a mass of crystals is deposited, which is purified from traces of anilotic acid by means of ether, and then crystallized by solution in hot water. When pure it does not alter the colour of sesquichloride of iron, but the smallest trace of anilotic acid turns that salt blood-red.

The composition of helicine is very remarkable. In the anhydrous state it is $C_{26}H_{16}O_{14}$, and the crystals contain besides, for 2 eq. of helicine, 3 eq. of water. This formula differs only by 2 eq. of hydrogen from that of salicine, and it appears to be well ascertained by Piria, that in its formation the saligenine of the salicine has been converted into hyduret of salicylic acid, which, combining with the sugar, has yielded the helicine. In fact, helicine is decomposed by heat, yielding hyduret of salicylic acid; by alkalis, forming metallic salicylurets; by strong acids, yielding sugar and hyduret of salicylic acid; and by synaptase, with the same result.

Helicoidine.—When a still weaker nitric acid is employed, acid, for example, of sp. gr. 1·080, salicine yields another crystalline compound, resembling helicinc, named by Piria *helicoidine*. It is the result of a still less complete oxidation, for it is found to consist of



which is the formula of anhydrous *helicoidine*: the crystals contain, besides, 3 eq. of water. *Helicoidine* is evidently a combination of the elements of *helicine* with those of unaltered *salicine*, but Piria has shewn that *salicine* is not present in it as such.

Chlorohelicine.—By the action of chlorine on *helicine* suspended in water, there is formed this compound, in which 1 eq. of hydrogen in the hyduret of salicyl of the *helicine* is replaced by chlorine. In other words, *chlorohelicine* is a compound of sugar $C_{12}H_{10}O_{10}$, and chlorosalicylic acid $C_{14}\left\{\begin{smallmatrix} H_5 \\ Cl \end{smallmatrix}\right\}O_4$, and it exhibits all the characters of such a compound.

Bromohelicine.—This is a compound analogous to the preceding one, and is obtained by the action of bromine on *helicine*. Its formula is of course $C_{26}H_{15}BrO_{14}$, and it contains sugar $C_{12}H_{10}O_{10}$, and bromosalicylic acid $C_{14}\left\{\begin{smallmatrix} H_5 \\ Br \end{smallmatrix}\right\}O_4$.

Rutiline.—Braconnot has thus named the product of the decomposition of *salicine* by strong sulphuric acid. When pure, it is brownish-red, with a tinge of yellow while moist, dark-brown when dry; brittle, tasteless, insoluble in water and alcohol. Strong acids colour it of a fine blood-red; alkalies of a deep violet. It is derived from the *saligenine*, but its formation and composition have not been fully studied.

PHLORIDZINE.

Discovered by De Koninck in the fresh bark of the root of the apple, pear, cherry, and plum tree. In its characters it is closely connected with *salicine*, but it is not yet so well known. When *salicine* was believed to be $C_{42}H_{29}O_{22}$, *phloridzine* was said to have the formula $C_{42}H_{29}O_{24}$, and, therefore, to contain only 2 eq. of oxygen more; but, as the formula of *salicine* has now been altered, and seems really to be ascertained, it is probable that of *phloridzine* will also have to be changed.

It is extracted from the bark by boiling alcohol of 80 p. c. The

alcohol is distilled off, and the phloridzine crystallizes out of the residual liquid.

It forms fine, colourless, four-sided silky needles, soluble in 1000 parts of cold water, and in every proportion in boiling water. The solution has a bitter, slightly astringent taste. It is soluble in alcohol, and sparingly soluble in ether. Sp. gr. 1.4298. At 212° it loses 4 at. water of crystallization, it melts at 300° , and is decomposed at 384° . A solution of phloridzine gives, with subacetate of lead, a white precipitate, which, according to Mulder, is 1 at. of anhydrous phloridzine combined with 6 at. of oxide of lead.

Phloridzine is acted on by dilute acids exactly as salicine is. Both substances have been used with success in intermittents.

PRODUCTS OF THE DECOMPOSITION OF PHLORIDZINE.

PHLORETINE.

Discovered by Stass. When a solution of phloridzine in water is boiled with the addition of a little muriatic or sulphuric acid, it is converted, in a manner precisely similar to salicine, into grape sugar and phloretine. This body is analogous to saliretine. Phloretine crystallizes in plates, of a sweet taste, slightly soluble in water and in ether, very soluble in alcohol, concentrated acetic acid, alkalies, sulphuric acid, and muriatic acid.

Its formula is $C_{30}H_{15}O_{10}$.

PHLORIDZEINE.

Discovered by Stass. When phloridzine is moistened with ammonia and exposed to the atmosphere, it acquires a blue colour, by the absorption of oxygen, and may be dissolved in an excess of ammonia. A red powder is precipitated from the solution on the addition of acids, which is the substance named phloridzeine. Its formula is said to be $C_{42}H_{29}O_{26}N_2$, and it is supposed to be derived from phloridzine, by the separation of 6 atoms of water, and combination of 8 atoms of oxygen, and 2 equivalents of ammonia. Its solution in ammonia gives by evaporation a purple-red mass, the surface of which has the metallic lustre and colour of copper. It remains unchanged in the air, and is easily soluble in water, forming a solution of a splendid blue colour. Sulphuretted hydrogen and other substances, which have an attraction for oxygen, decolorize it, but the colour is restored on exposure to air, by the absorption of oxygen.

CINNAMYLE.

The hypothetical radical of oil of cinnamon and of cinnamic acid. According to the researches of Dumas and Peligot, Ceylonese oil of cinnamon is composed according to the formula $C_{18}H_8O_2$; and by absorbing 2 at. oxygen from the atmosphere, is converted into cinnamic acid. Oil of cinnamon forms with nitric acid a compound which crystallizes in oblique rhombic prisms, consisting of an equal number of atoms of oil of cinnamon, nitric acid, and water. With hydrochloric acid it forms a green solid mass, composed of an equal number of equivalents of the anhydrous oil and of hydrochloric acid. With ammonia it forms a solid friable mass, also composed of one equivalent of each substance.

Formula of cinnamyle, $C_{18}H_7O_2$; Symbol, Ci.

Chlorine decomposes the oil of cinnamon, forming a liquid compound, and another which sublimes in long white needles. The latter has the formula $C_{18}H_4Cl_4O_2$; and consequently it is oil of cinnamon in which half the hydrogen has been replaced by its equivalent of chlorine. There is here some analogy with the compounds of benzoyle; but there are also great differences, which may be explained by the fact, that, according to Blanchet and Sell, the oil of cinnamon consists of two distinct oils, one heavier, and one lighter than water. The heavier has at 77° a sp. gr. of 1.008, and boils at 430° . If the commercial oil be treated with barytic water, a saline combination of the heavy oil is produced, which is soluble in water, and from which the heavy oil is separated by acids. The lighter oil may be distilled from the mixture of the commercial oil with baryta.

According to a late investigation by Mulder, the composition of the oil of cinnamon of Ceylon, Java, and China, and the oil of cassia flowers and cassia bark, is represented by the formula $C_{20}H_{11}O_2 = 1$ eq.: the combination with hydrochloric acid contains 1 eq. of that acid; that with ammonia 1 eq. ammonia. The oil of cassia flowers combines only with half as much ammonia. Blanchet's analysis of Ceylon oil of cinnamon gave a result closely approximating to that of Mulder; but Dumas, on repeating his earlier analyses, found reason to dispute the correctness of Mulder's formula. As the difference in the proportion of hydrogen in the analyses of Dumas and Mulder is above 1 per cent., which cannot arise from an error in the manipulation, we are led to consider the existence of two oils as highly probable; but it appears that the oil $C_{20}H_{11}O_2$, when acted on by the oxygen of the air, may yield either cinnamic acid and two resins, or hyduret of cinna-

myle and two resins; and these are the substances usually found in the oil of commerce. In the meantime it may be considered as certain, that the oil which forms with nitric acid the crystalline compound above mentioned, has the formula $C_{18}H_8O_2$. (Dumas.)

OIL OF CINNAMON OR CASSIA.

Obtained by distilling the bark of *Laurus cinnamomum* and the bark and flowers of cassia. It is a yellow oil, heavier than water, possessing the odour of cinnamon, solid below 32° , melting at 23° . It has a pungent, burning, sweetish taste; deposits crystals when kept, and when exposed to the air becomes brown, and passes into cinnamic acid. It is sparingly soluble in water, forming cinnamon water. This solution, mixed with iodine and iodide of potassium, yields brilliant reddish-brown crystals of a strong metallic lustre; the probable composition of which, according to Apjohn, is $KI + I_3C_6H_5 = KI + (C_{18}H_7O_2 + H) + I_3$, corresponding in 100 parts to 12.26 iodide of potassium, 28.08 iodine, and 59.66 oil of cinnamon. To obtain these crystals, 240 grains of iodide of potassium, and 10 grains of iodine, dissolved in a little water, are added to 2 lb. of cinnamon water, and the mixture exposed to a temperature of 32° , when the crystals form. They are soluble in ether and alcohol without alteration, but are decomposed by water. (Apjohn.)

Aqua potassæ dissolves oil of cinnamon easily and completely, and diluted acid separates it again unchanged from the solution. If the solution of the oil in potash be distilled, an oil passes over with the vapour of water, which is lighter than water, has an odour of cinnamon and bitter almonds, and is composed according to the formula $C_{18}H_{10}O_2$: the residue contains benzoate of potash, mixed with a black matter. (Mulder.) Oil of cinnamon, heated with hydrate of potash, gives off hydrogen gas, and cinnamic acid is probably formed. The oil, if mixed with nitric acid in the cold, becomes thick, and is wholly or partially converted into a crystalline mass. If boiled with nitric acid, the smell of oil of bitter almonds is perceived, and benzoic acid is found in the residue. Benzoic acid is also formed by the action of hypochlorites on the oil of cinnamon. Ammoniacal gas solidifies the oil, producing undoubtedly several bodies; one of which is soluble in alcohol and ether, and crystallizes in fine silky needles grouped together. The composition of these substances has not been examined.

CINNAMIC ACID.

Discovered by Dumas and Peligot. It is formed in hard translucent prisms, when oil of cinnamon is long exposed to the atmosphere. It may also be easily obtained by dissolving in potash the oil of balsam of Peru (see that article) with a gentle heat, evaporating to dryness, dissolving the residue of cinnamate of potash in boiling water, and adding an excess of hydrochloric acid; the cinnamic acid crystallizes on cooling, and is purified by repeated crystallization. It is most economically extracted from liquid storax by boiling with caustic potash or soda, precipitating by an acid, and purifying the crystals of cinnamic acid from resin by repeated solution in hot water and crystallization. Colourless, transparent scales, having a weak aromatic taste; less soluble in hot and cold water than benzoic acid. It crystallizes from alcohol in colourless rhombic prisms, which are hard and friable, fusible at 240° , boiling at 555° , and distilling as a heavy oil, which consolidates on the neck of the retort to a white crystalline mass. By the action of nitric acid it is converted into hyduret of benzoyle, and a crystallizable acid which has very nearly the same composition as benzoic acid, but is easily distinguished from that acid by its salts. The probable formula of this new acid is $C_{15}H_5O_3$. (Plantamour.) This reaction is unexplained. By the action of cold nitric acid on cinnamic acid there is formed a new acid, nitrocinnamic acid, in which 1 eq. of hydrogen is replaced by nitrous acid. It forms detonating salts, and the nitrocinnamate of oxide of ethyle is a crystallizable ether. The formula of nitrocinnamic acid is $C_{18}\left\{\begin{matrix} H_6 \\ NO_4 \end{matrix}\right\}O_3,HO$.

The formula of cinnamic acid is $C_{18}H_7O_3,HO$; Symbol, ClO,HO .

By the action of heat, cinnamic acid is decomposed, yielding the remarkable carbo-hydrogen found in storax, and hence called styrole, the formula of which is $C_{16}H_8$. In its formation from cinnamic acid, the acid $C_{18}H_8O_4$, yields 2 eq. carbonic and 1 eq. styrole.

Styrole.—This compound was first obtained by Simon from liquid storax by distillation with water. It is probable that it is derived from cinnamic acid, which is always present in storax.

Styrole, when rectified, is a colourless mobile oil, refracting light strongly. It has been studied by Hoffmann and Blyth, who ascertained its formula to be $C_{16}H_8$. When heated in a sealed tube to nearly 400° , it very soon becomes solid, and is converted into an isomeric modification, *metastyrole*. The same change takes place more slowly

at low temperatures. Metastyrole, if more strongly heated, is reconverted into styrole, which distils.

Styrole is analogous to benzole, and like it forms with nitric acid a peculiar compound, *nitrostyrole*, $C_{16}\left\{\begin{smallmatrix} H_7 \\ NO_4 \end{smallmatrix}\right\}$. With bromine styrole instantly forms a crystalline body, *bromide of styrole*, which appears to be a direct compound of styrole with 2 eq. of bromine, $C_{16}H_8Br_2$. Chlorine forms an analogous compound, which is liquid, the chloride of styrole, $C_{16}H_8Cl_2$.

Metastyrole, when acted on by nitric acid, yields a solid compound, *nitrometrastyrole*, the formula of which is $C_{14}\left\{\begin{smallmatrix} H_6 \\ NO_4 \end{smallmatrix}\right\}$. If we suppose this to be derived from metastyrole as nitrostyrole is from styrole, then the true formula of metastyrole will be $C_{14}H_7$, which is the same proportion as $C_{16}H_8$; and if this be the case, then the very remarkable change of styrole into metastyrole is the result of the equivalent of styrole being reduced by $\frac{1}{8}$. In other words, if the molecule of styrole contain 8 molecules of C_2H , that of metastyrole will contain only 7.

For further details on these very remarkable compounds, the reader is referred to the memoir of Hoffman and Blyth in the "Annalen der Chemie und Pharmacie," liii. 289. For the fact of the production of styrole from cinnamic acid we are indebted to Hempel. (Annalen, lix. 316.)

SALTS OF CINNAMIC ACID.

Cinnamic acid forms with metallic oxides salts which, in general, are analogous to the benzoates. In these salts 1 at. of basic water in the acid is replaced by the oxide. Cinnamate of silver, obtained by mixing a solution of neutral cinnamate of potash with nitrate of silver, is a white, flocculent, amorphous precipitate, which becomes black in boiling water.

HYDURET OF CINNAMYLE.

Discovered by Dumas and Peligot. Obtained by putting freshly prepared nitrate of hydurate of cinnamyle in contact with water, when the nitric acid combines with the water, and the hyduret of cinnamyle separates. It is an oily liquid; which, if again placed in contact with nitric acid, solidifies instantly and completely. It seems to be the chief ingredient in oil of cinnamon.

Formula, $C_{18}H_8O_2$, or $C_{18}H_7O_2 + H$; Symbol, CiH .

CHLORINE AND OIL OF CINNAMON.

The action of chlorine on Chinese oil of cinnamon gives rise to several new products. Heat is developed, much hydrochloric acid gas is given off; the oil becomes at first brown, afterwards colourless, and thickens. If the oil be distilled in a stream of chlorine, the portion which first passes over is colourless, very fluid, and instantly converted by liquor potassæ into a soluble crystalline mass. This fluid oil may be mixed with sulphuric acid without decomposition. If left to itself for some time, it solidifies into a crystalline mass, which seems to be benzoic acid. After this fluid oil, there distils a brown oil, which possesses in a less degree the same property, and when treated with liquor potassæ leaves undissolved an oily body containing chlorine. If the products of this distillation are repeatedly exposed to the action of chlorine at a high temperature, there are at least obtained a black coaly residue, and a volatile white crystalline substance, which is very fusible, and unaltered by oil of vitriol, or by distillation in ammoniacal gas. Its formula is $C_{18}H_4Cl_4O_2$. Dumas and Peligot have named it Chlo-rocinnose.

APPENDIX TO THE COMPOUNDS OF CINNAMYLE.

OIL OF BALSAM OF PERU.

The balsams of Peru and Tolu contain compounds which belong to the series of cinnamyle.

According to Stoltz and Wernher, 2 vol. of balsam of Peru, and 3 vol. of aqua potassæ sp. gr. 1·300, when heated together, produce a yellow or yellowish-brown oil, (oil of balsam of Peru.) which swims above a dark brown or black syrupy liquid, soluble in water, which contains all the potash.

The former is purified by distillation, leaving a slightly carbonaceous residue. It is then clear and colourless. Fremy calls it Cinnameine; its probable formula is $C_{144}H_{65}O_{20}$. According to Plantamour and Fremy, this substance, which is allied to the fat oils, when boiled with alkalies, produces cinnamic acid, which combines with the alkali, and a neutral substance, just as in the saponification of fat oils. The latter substance is peruvine. When a solution of the oil of Peru balsam in alcohol is mixed with an alcoholic solution of potash, it instantly solidifies into a micaceous mass of cinnamate of potash. After the alcohol has been distilled off by the application of a gentle heat, the alkaline

residue by distillation with water yields at first a clear and colourless oil, heavier than water, which from its reactions and composition appears to be cinnamic ether, (cinnamate of oxide of ethyle,) the production of which in these circumstances is very remarkable. The latter product of the distillation is peruvine.

Peruvine is a colourless oily fluid, lighter than water, refracting light powerfully. Its composition approaches to $C_{18}H_{12}O_2$. According to this formula, 1 at. cinnamine produces 3 at. cinnamic acid and 2 at. peruvine.

When dry hydrate of potash is employed instead of the aqueous or alcoholic solution of potash, the cinnamine is decomposed in a different manner. Hydrogen gas is given off, while cinnamate of potash is formed.

When cinnamine is exposed to a cold of $+26^{\circ}$, it deposits neutral crystals, soluble in alcohol and ether, the formula of which is $C_{18}H_8O_2$, exactly that of hyduret of cinnamyle. This substance, therefore, is isomeric with hyduret of cinnamyle, as benzoine is with hyduret of benzoyle.

Cinnamine, mixed with oil of vitriol, is converted into a brown, resinous matter, which appears to be a compound of 1 at. cinnamine and 7 at. water.

By the action of chlorine, cinnamine is converted into chloride of benzoyle, and an oily fluid, containing no chlorine, which cannot be separated from it.

According to Richter, the oil of balsam of Peru consists of two distinct oils, which may be separated by agitation with 2 vol. of alcohol at 75 p. c. The oil soluble in such alcohol he calls Myriospermine; the other, which is insoluble, Myroxiline.

Myroxiline.—Richter dissolves in absolute alcohol the brown oil left after continued agitation with weak alcohol, and exposes the solution in weak alcohol to the freezing temperature, whereby some of the brown oil separates, which is added to the solution in absolute alcohol. This solution, mixed with water, is now left to spontaneous evaporation, when the myroxiline at the temperature of 42° crystallizes in tallowy masses grouped in a circular form. The specific gravity of myroxiline is 1.111. By the action of liquor potassæ it produces cinnamic acid and a resinoid substance.

Myriospermine.—The spirituous solution containing the myriospermine being evaporated, that substance is left as an oil nearly colourless, possessing a great refracting power. It crystallizes from a concentrated solution in alcohol of 75 p. c. at the temperature of from $+14^{\circ}$ to $+3^{\circ}$, in fine needles grouped together, which contain alcohol. Accord-

ing to Richter, myriospermine is converted by the action of an alcoholic solution of potash into an acid, which differs from cinnamic acid essentially in its capacity of saturation. The atomic weight of this acid, in its compound with oxide of silver, according to him is 1553·85 ($0 = 100\cdot00$). (Richter in Erdmann's Journal, t. xiii. p. 175.)

BALSAM OF TOLU.

According to the recent researches of Deville, balsam of Tolu contains benzoic acid and a body isomeric with hyduret of benzoyle; also cinnameine; hence it agrees in many points with balsam of Peru. It contains, moreover, several resins, and finally yields, when distilled, a remarkable carbohydrogen, toluole or benzoène.

Toluole. Syn. Benzoène.—This oil is analogous to benzole and styrole. Its formula is $C_{14}H_8$, and it therefore probably belongs to the series of benzoyle. Indeed, in one sense it may be viewed as the foundation of that series, the chief members of which may be supposed to be derived from it by substitution.

Thus we have

Toluole	.	.	.	.	.	$C_{14}H_8$.
Hyduret of Benzoyle	.	.	.	.	.	$C_{14} \left\{ \begin{array}{l} H_6 \\ O_2 \end{array} \right.$
Anhydrous Benzoic Acid	.	.	.	.	.	$C_{14} \left\{ \begin{array}{l} H_5 \\ O_2 \end{array} \right.$
Benzamide	.	.	.	.	.	$C_{14} \left\{ \begin{array}{l} H_5 \\ NH_2 \\ O_2 \end{array} \right.$

We shall see hereafter that benzole, in like manner, may be viewed as the foundation of a series.

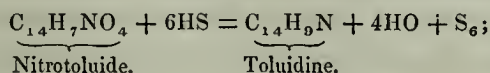
By the action of nitric acid toluole is converted into *nitrotoluide*, a body analogous to nitrobenzide, in which, therefore, 1 eq. of hydrogen is replaced by nitrous acid. It has also been called *protonitrobenzoène*. It is a liquid which, when passed in vapour over red-hot lime, is converted into aniline, $C_{12}NH_7$, and carbonic acid.

$$\text{Nitrotoluide is} \quad . \quad . \quad . \quad . \quad . \quad C_{14} \left\{ \begin{array}{l} H_7 \\ NO_4 \end{array} \right\} = C_{14}NH_7O_4;$$

$$\text{and, if we subtract from this 2 eqs. of Carbonic Acid} \quad . \quad . \quad C_2 \quad O_4,$$

$$\text{there remains 1 eq. Aniline} \quad . \quad . \quad . \quad . \quad . \quad C_{12}NH_7.$$

When nitrotoluide is acted on by sulphuretted hydrogen, ammonia being present in excess, it yields a new base, *toluidine*, to which we shall return in treating of organic bases. Toluidine is $C_{14}H_9N$, and its production from nitrotoluide $C_{14}NH_7O_4$ is thus explained:—



that is, of 6 eq. of hydrogen, derived from sulphuretted hydrogen, 4 eq. remove the 4 eq. of oxygen from the nitrotoluide, while 2 eq. unite with the residue to form toluidine, and 6 eq. of sulphur are set free. The whole reaction corresponds exactly to that in which aniline $C_{12}H_7N$ is formed from nitrobenzide $C_{12}H_5NO_4$.

By the further action of nitric acid nitrotoluide is converted into a crystalline solid body, analogous to dinitrobenzole, in which, therefore, 2 eq. of hydrogen are replaced by nitrous acid. Its formula is $C_{14}\left\{\begin{smallmatrix} H_6 \\ 2NO_4 \end{smallmatrix}\right\} = C_{14}N_2H_6O_8$. It may be called *dinitrotoluide*.

Toluole, when acted on by chlorine, yields a series of compounds in which hydrogen is replaced by chlorine, which enter into combination with the hydrochloric acid formed along with them.

With sulphuric acid toluole yields a new acid, $C_{14}H_7S_2O_5$, in which 1 eq. hydrogen seems to be replaced by 1 eq. hyposulphuric acid.

Besides toluole, balsam of tolu contains another carbohydrogen, $C_{24}H_{18}$, which has been called *tolene*. It is more volatile than toluole, but does not appear to have been particularly studied.

ANISYLE.

This name is given by Cahours to the hypothetical radical of a series of compounds derived from oil of anise, (*Pimpinella anisum*), which are very analogous to the compounds of benzoyle.

Oil of anise, like some other oils, contains two compounds, a liquid and a solid, which are isomeric. The solid oil of anise is the most abundant, and from it the following compounds have been derived. Its formula is $C_{20}H_{12}O_2$. When acted on by diluted nitric acid, it yields *anisic acid* and *hyduret of anisyle*. Sulphuric acid converts it into a solid body, *anisoine*, which was at first supposed to be isomeric with the oil; but which is now said to be isomeric with hyduret of anisyle, as benzoine is with hyduret of benzoyle. Whichever view be the correct one, it affords a good example of the production of an isomeric or polymeric modification of an organic compound.

Hyduret of Anisyle.—This is an amber-yellow oil, of sp. gr. 1.09, of a burning taste and aromatic smell, like that of hay. Its formula is $C_{16}H_8O_4 = H + C_{16}H_7O_4$. Bromine converts it into bromanisyle, $Br + C_{16}H_7O_4$. Ammonia produces with it a compound analogous to salicylimide, which Cahours has called Anishydramide. Three eq. hyduret of anisyle and 2 eq. ammonia yield 6 eq. water, and 1 eq. of the new body, which form brilliant crystals, of the formula $C_{48}N_2H_{24}O_6$.

Anisic Acid.—By the action of melted potash hyduret of anisyle is

converted, with disengagement of hydrogen, into anisic acid, $C_{16}H_8O_6$, $= C_{16}H_7O_5.HO$, entirely analogous to salicylic acid. It is remarkable that this acid is isomeric with the oil of gaultheria, which is the salicylate of oxide of methyle, $C_{16}H_8O_6 = C_2H_3O + C_{14}H_5O_5$.

Anisic acid forms well characterized and crystallizable salts with bases.

Bromine converts anisic acid into *bromanisic acid*, $C_{16}\left\{\begin{smallmatrix} H_7 \\ Br \end{smallmatrix}\right\}O_6$.

Chlorine forms a similar compound, *chloranisic acid*, $C_{16}\left\{\begin{smallmatrix} H_7 \\ Cl \end{smallmatrix}\right\}O_6$.

When oil of anise is acted on by strong nitric acid, there is formed *nitranisic acid*, $C_{16}\left\{\begin{smallmatrix} H_7 \\ NO_4 \end{smallmatrix}\right\}O_6$.

Anisole.—When anisic acid is heated with lime or baryta, it yields carbonate of the base and an oil called anisole, the formula of which is $C_{14}H_8O_2$, differing from that of anisic acid by 2 eq. of carbonic acid, as benzoic does from benzoic acid.

Anisole is acted on by chlorine, bromine, and nitric acid, yielding products which, in all probability, are analogous to those derived from benzole and styrole.

It has been recently shewn by Cahours that the salicylate of oxide of methyle, (oil of gaultheria,) when heated with baryta, yields anisole, which is explained by its being isomeric with anisic acid.

Gerhardt has also demonstrated that anisic acid and anisole are identical with draconic acid and dracole, compounds obtained by Laurent from the oil of estragon. He has also shewn that this latter oil is identical with oil of anise. Cahours has proved that the solid oils of fennel (*Anethum fœniculum*), of *Ilicium anisatum*, and of bitter fennel are all identical with that of anise.

GUAIACYLE.

This name has been given to the hypothetical radical of an oil obtained from the gum resin guaiacum. This oil, like that of spiræa, has acid properties, and has indeed been described as pyroguaiacic acid. It is supposed to be a hyduret of guaiacyle; and as this supposed hyduret is $C_{14}H_8O_4$, guaiacyle will be $C_{14}H_7O_4$. It therefore differs from salicyle by only 2 eq. of hydrogen, and the same difference exists between the hydurets.

Hyduret of guaiacyle, $C_{14}H_8O_4 = C_{14}H_7O_4 + H$, is a colourless oil, which, as already stated, has acid properties. It is isomeric with saligenine; and it would be curious to ascertain whether any

direct relation can be traced between these two compounds, the origin of which is so different, and which, when decomposed, yield, as far as we know, different products.

Guaiacic Acid.—The acid corresponding to benzoic, salicylic, and cinnamic acids, the formula of which as hydrate would be $C_{14}H_8O_6$, has not yet been obtained, but Thierry has given this name to another acid, $C_{12}H_8O_6 = C_{12}H_7O_5, HO$. This last acid, when we subtract from its formula 2 eq. of carbonic acid, gives $C_{10}H_8O_2$, and this is the composition of a neutral oil found by Deville among the products of the distillation of guaiacum. This oil has been called guaiacène.

RADICALS FORMING BASES.

ETHYLE.

ETHYLE is the hypothetical radical of the ethers. It has not yet been obtained in a separate form. With 1 eq. oxygen ethyle forms ether, the oxide of ethyle, which possesses the properties of a base. Alcohol is the hydrate of oxide of ethyle. The formula of ethyle is C_4H_5 ; Symbol, Ae.

ETHYLE AND OXYGEN.

Oxide of Ethyle. Syn. Ether; Sulphuric Ether.—Formula, C_4H_5O ; Symb. AeO. A mixture of ether and alcohol seems to have been known even in the thirteenth and fifteenth centuries. But Valerius Cordus first published, in 1544, precise directions for making ether, according to which a mixture of equal weights of alcohol and oil of vitriol is to be distilled; a process still frequently employed. The preparation of ether seems after this to have sunk into oblivion, till Frobenius in 1729 anew described it.

Ether is formed by the decomposition of the bisulphate, biphosphate, and binarsenate of oxide of ethyle (sulphovinic, phosphovinic, and arseniovinic acids), and by the action of fluoride of boron, chloride of zinc, chloride of tin, and other chlorides, on alcohol.

Prep.—Five parts of alcohol of 90 p. c. are mixed with 9 parts of oil of vitriol in a vessel of copper or iron placed in cold water. The mixture is now introduced into a still, and by means of a strong fire is kept in a state of continued ebullition. The vapour of ether distils

along with those of water and alcohol, and all are condensed in an efficient cooling apparatus. A quantity of alcohol of the same strength, equal in bulk to the liquids distilled off, is to be added to the liquid in the still, and the operation repeated. To the distilled liquid is now added so much of an alcoholic solution of potash as causes a perceptible alkaline reaction; and it is then rectified by distillation in the water-bath as long as the ether, which distils over, has a sp. gr. of 0.720 to 0.725 at 80° F. Or before rectification it may be mixed with a little milk of lime and its own bulk of water. By allowing it to stand for some days over chloride of calcium or quicklime, and a new rectification in contact with one of these substances, it is obtained perfectly pure.

On the large scale, a given quantity of oil of vitriol may be made to convert an almost unlimited quantity of alcohol into ether. The mixture of oil of vitriol and alcohol of 90 p. c. as above, being introduced into the retort or still, is connected with a vessel full of the same alcohol by means of a syphon-tube, furnished with a stop-cock, and passing through the tubulure of the retort. The longer limb of the syphon is so arranged as just to dip into the liquid in the retort. As soon as full ebullition is going on, the stopcock is opened, so as to allow alcohol to flow into the retort in such a manner as to keep the boiling liquid exactly at the same level; that is, to supply a volume of alcohol equal to that of the liquid which distils over. If the operation be well managed, the whole of the alcohol which enters the retort passes off as ether and water; and the oil of vitriol continues for a long time to produce this decomposition without losing any of its power. In fact, it would continue to do so for an indefinite time, were it not that it is gradually diluted by the superfluous water contained in alcohol of 90 p. c.; and when diluted to a certain degree, it can no longer produce ether. For the explanation of what takes place in this interesting process, see below (Products of the decomposition of bisulphate of oxide of ethyle, or sulphovinic acid).

Ether is a colourless, clear, and very mobile liquid; and has the sp. gr. 0.7119 at 75°, 0.7154 at 68°, and 0.7237 at 55°. It refracts light strongly, is a non-conductor of electricity, boils at 96°, yielding vapour of sp. gr. 2.565, and freezes at from —24° to —45°. By its evaporation an intense cold is produced. It has a pleasant, penetrating, ethereal odour; its taste is cooling (from its quick evaporation), penetrating, and aromatic. It is highly inflammable; and its vapour, mixed with oxygen or atmospheric air, forms a very dangerous explosive mixture. It dissolves in 10 parts of water, and is miscible with alcohol and the fatty and volatile oils in all proportions. When kept in ves-

sels containing air, ether, by absorption of oxygen, is partly converted into acetic acid and water, and becomes acid to test paper. This latter effect is also sometimes owing to the presence of sulphurous acid, which gradually passes into sulphuric acid, or which proceeds from the decomposition of a little oil of wine which has distilled over with it.

At a higher temperature, ether rapidly absorbs oxygen, producing acetic, formic, and lampic (aldehydic) acids; the last of which is known by its suffocating smell, and its power of causing a flow of tears from the eyes. When passed through a red-hot glass tube, ether is resolved into aldehyde, olefiant gas, and marsh gas (light carburetted hydrogen). Ether dissolves $\frac{1}{80}$ th of sulphur and $\frac{1}{37}$ th of phosphorus. Bromine and iodine are dissolved by it in quantity, but with decomposition; hydrobromic and hydriodic acids are produced, along with other products not yet examined. Chlorine gas, passed through ether, instantly decomposes it; at the ordinary temperature each bubble inflames, while hydrochloric acid and carbon are produced. If the ether be cooled, there is formed, besides hydrochloric acid, a fluid compound, containing chlorine, which with potash produces chloride of potassium and acetate of potash. (Malaguti.) Anhydrous sulphuric acid decomposes ether in two ways. In the cold are produced isethionic and althionic acids, sulphate of oxide of ethyle, oil of wine, and bisulphate of oxide of ethyle. But if heat be employed, these products are decomposed; and sulphate of oxide of ethyle, oil of wine, water, and ether, accompanied by acetic, formic, and sulphurous acids, carbonic oxide, and olefiant gas, distil over.

Nitric acid, with the aid of heat, converts ether into aldehyde, with acetic, formic, oxalic, and carbonic acids. If oxygen from nitric acid be added to the elements of ether, we obtain from

Oxygen	.	.	1 at. Ether = C_4H_5O .
2 atoms	.	.	1 at. Aldehyde, and 2 at. Water.
4 atoms	.	.	1 at. Acetic Acid, and 2 at. Water.
8 atoms	.	.	2 at. Formic Acid, and 3 at. Water.
10 atoms	.	.	2 at. Oxalic Acid, and 5 at. Water.
12 atoms	.	.	4 at. Carbonic Acid, and 5 at. Water.

Hydrochloric acid is greedily absorbed by ether, and the concentrated solution when distilled yields chloride of ethyle. Anhydrous alkalis have no action on pure ether at the ordinary temperature; but if water and air are present, the ether becomes brown; and after some time the alkali is found to be in part combined with acetic and formic acids, formed by oxidation. The brown substance appears to be formed by the decomposition of aldehyde.

Potassium and sodium decompose ether by depriving it of oxygen, although slowly and imperfectly. There are formed in this reaction

gaseous and oily carbo-hydrogens. The oxides of potassium and sodium when formed combine with undecomposed ether, forming saline compounds. Lead, zinc, and iron, when in contact with ether, cause the absorption of oxygen and the production of acetates of the metallic oxides.

Oxide of ethyle (ether) combines with water to form alcohol (hydrate of oxide of ethyle); and with acids, forming neutral and acid salts. The acid salts are commonly named acids, as sulphovinic and phosphovinic acids; the neutral salts are called compound ethers, as oxalic ether, &c.

Ether is used in medicine: internally as a diffusible stimulant; externally to produce cold by its evaporation, and also in frictions. When the vapour of ether, mixed with air, is inhaled, it produces a species of coma, the most striking feature of which is insensibility to pain. In many cases, severe operations may be performed without any indications of suffering on the part of the patients. In others there is some appearance of pain and suffering, even severe, but on awaking the patient has no recollection of having felt anything of the kind. In these cases, there has been, therefore, not insensibility to pain, strictly speaking, but only divided consciousness. It might be supposed that in such cases the shock to the system would be the same, whether the patient remembered the pain or not, if he really felt it; but this does not appear to be the case; for the ether has been successfully employed not only in operations, but in parturition; and while it has not interrupted the action of the uterus, it has apparently very much accelerated the recovery, even where, at the time, pain seemed to be felt, but was not remembered. Care must be taken, in the administration of ether in this way, not to approach a light to the vessel or to the mouth of the patient; since the vapour of ether is highly inflammable, and, when mixed with air, forms an explosive mixture; and thus serious or even fatal accidents might happen. When inhaled, also, the vapour of ether must be mixed with a proper amount of air; for the pure vapour of ether is irrespirable, and, if introduced into the lungs, would tend to cause asphyxia. In pharmacy, ether is also sometimes employed as a solvent for phosphorus, sulphur, iodine, sesquichloride of iron, and ammonia. It is the best solvent of the fixed oils and fats.

Pure ether should be clear and colourless, neutral to test paper, and of sp. gr. not more than 0.73 at 68° for medical use. It should not become milky when mixed with water, and should not dissolve in less than 10 parts of water.

OXIDE OF ETHYLE WITH WATER.

Syn. Alcohol; Hydrate of Oxide of Ethyle.—Formula, $C_4H_6O_2$: Symbol, $AeO + HO$, &c.

Alcohol is formed by long contact between ether and water, which combine very slowly; but these substances combine instantly when presented to each other in the nascent state. This takes place, for example, when the acid salts of oxide of ethyle are heated with water; when the neutral salts of oxide of ethyle, or the haloid salts of ethyle, are decomposed by being heated with the hydrated alkalies; when the double salts of oxide of ethyle with lime or baryta are gently heated; and in the peculiar decomposition of sugar which constitutes the vinous fermentation.

By the distillation of all liquids which have undergone the vinous fermentation there is obtained a more or less diluted alcohol, the strength of which is indicated by its specific gravity. A liquid containing 50 to 52 per cent. of alcohol is called spirits (brandy, &c.): its sp. gr. is 0.95 or 0.94. Rectified spirit of wine contains from 66 to 70 per cent., and has a sp. gr. of 0.89 to 0.88. The most highly rectified spirit of wine, the sp. g. of which is 0.835 to 0.840, contains about 90 per cent. of alcohol. All these specific gravities are referred to a temperature of 60°.

Absolute alcohol is obtained by saturating spirits of 90 per cent. with fused chloride of calcium, and distilling the solution; the water remains behind in combination with the chloride of calcium. Quicklime and dry carbonate of potash may be employed for the same purpose. According to Graham, alcohol of 90 p. c. is placed under the exhausted receiver of the air-pump near a vessel containing quicklime. In the course of a few days the alcohol is deprived of the water which it contains. Lastly, alcohol of 90 per cent. is placed in a bladder, which is suspended in a warm place. The water moistens the bladder, and evaporates from the external surface, while the alcohol is left. In this way it may be brought to 98 per cent., but with some loss, as alcohol escapes through the upper part of the bladder, which is not in contact with the liquid.

Alcohol, as obtained from brandy or whisky, has a peculiar odour, derived from the presence of an essential oil. This is best removed on the small scale by rectification with a little caustic potash, (Göbel, Liebig,) or by digesting the spirits with freshly ignited pine charcoal.

Pure alcohol is a clear, colourless, mobile liquid; sp. gr. 0.792—0.791 at 68°, or 0.7947 at 60°. It boils at 172°, yielding vapour of

sp. gr. 1·6133, and has not been frozen by any cold hitherto produced. It refracts light powerfully, and is a non-conductor of electricity. The odour of alcohol is agreeable and penetrating, and it intoxicates powerfully. It is highly inflammable, and its combustion with a sufficient supply of oxygen yields only carbonic acid and water. If the supply of oxygen be deficient, it burns with a smoky flame. Alcohol greedily absorbs water from the atmosphere, and deprives animal substances of the water they contain, causing them to shrivel up. Hence its use in preserving anatomical preparations. Water and alcohol unite with disengagement of heat. Snow mixed with alcohol produces an intense cold. Great condensation attends the combination of alcohol and water. When 1 at. alcohol and 6 at. water are mixed, the bulk of the liquids contracts from 103·735 to 100 measures. Sp. gr. of this mixture, 0·920 at 60°. The boiling point of a mixture of alcohol and water rises with the proportion of water within certain limits. Alcohol of 94 p. c. has the same boiling point as pure alcohol; but alcohol from 96 to 99 p. c. boils at a somewhat lower temperature. Hence, in the preparation of absolute alcohol, the first portions which distil contain water, and are followed by absolute alcohol. For the percentage of alcohol in spirits of different densities, see the Table in the Appendix.

The purity of alcohol is known by its specific gravity. It should contain no essential oil, which may be detected by the addition of colourless oil of vitriol, which causes a red tinge if oil be present. According to Vogel, nitrate of silver is a still more delicate test for the oil, as when added to alcohol contaminated with this oil, and exposed to the sun's rays, it soon turns red; while no such effect is produced with pure alcohol. Alcohol should be neutral to test paper, and should leave no residue whatever on evaporation.

Alcohol, in the form of rectified spirit of wine, and proof spirit (equal volumes of alcohol at 90 p. c. and water), is extensively used in pharmacy, for the preparation of tinctures, spirits, &c. It is also employed as a powerful solvent for resins, oils, and vegetable alkalies, and in the preparation of ether and its compounds.

In the form of brandy and other ardent spirits, and of wine, it is much employed in medicine as a powerful diffusible stimulant, especially in diseases of a typhoid character.

ALCOHOL AND AMMONIA.

Alcohol absorbs ammoniacal gas readily. The alcohol ammoniatum of the pharmacopœia contains such a mixture, which is made by adding aqua ammoniæ to alcohol.

ALCOHOL AND IODINE.

Alcohol readily dissolves iodine, forming a dark brown solution,—tincture of iodine. The addition of water to the tincture causes nearly the whole of the iodine to separate in crystalline scales. Tincture of iodine is used in medicine; and, being a very powerful remedy, must be employed with caution.

ALCOHOL AND POTASH.

Alcohol dissolves caustic potash in the cold, and furnishes a method of purifying it from carbonate and sulphate, and chloride of potassium, all of which are left undissolved by the alcohol. If the alcoholic solution of potash be exposed to the atmosphere and warmed, it becomes brown, and is found to contain a substance apparently identical with resin of aldehyde, while acids, probably the acetic, formic, and aldehydic, are formed, and unite with the potash. When a mixture of equal parts of caustic lime and potash, moistened with alcohol, is subjected to distillation, pure hydrogen gas is evolved, and an acetate remains in the residue. (Dumas.)

ALCOHOL AND SALTS.

Alcohol dissolves many salts. Of inorganic salts, all those that are deliquescent in the atmosphere, with the exception of carbonate of potash, are soluble in alcohol. According to Graham, absolute alcohol combines with many salts, forming crystallizable compounds, which he calls alcoates, in which the alcohol performs functions analogous to those of hydratic (basic) water, and water of crystallization. These compounds are very easily decomposed.

Most of the organic acids are soluble in alcohol; and many of the salts which these acids form with inorganic bases, even those that are not deliquescent, dissolve easily in alcohol. Some of these solutions are used in medicine; as tincture of soap, and opodeldoc, which is a solution of hard soap in alcohol.

A mixture of alcohol and ether is used in medicine, under the name of spiritus vini æthereus.

Acids decompose alcohol; the oxygen acids by combining with the ether, the hydrogen acids by decomposing it. In the former case, acid salts of ethyle are formed; in the latter, compounds of ethyle with the radical of the acid. Potassium and sodium decompose the water of the hydrate of oxide of ethyle (alcohol); combining with its

oxygen, and disengaging hydrogen gas. The potash and soda which are formed produce crystallizable compounds with the oxide of ethyle (ether).

ETHYLE AND CHLORINE.

Chloride of Ethyle. Syn. Hydrochloric or Muriatic Ether.—

This compound is formed whenever alcohol is brought in contact with hydrochloric acid; and also by the action of many easily decomposed metallic chlorides, as sesquichloride of antimony, bichloride of tin, &c., on alcohol. In the latter cases, aldehyde is produced along with chloride of ethyle. It is best prepared by saturating alcohol with hydrochloric acid gas, and distilling in the water-bath. The distilled liquid is collected in a receiver, carefully cooled, and purified from alcohol and water by means of chloride of calcium. It must be preserved in stoppered bottles which are inverted.

Chloride of ethyle is a colourless liquid, having a penetrating aromatic odour, somewhat resembling that of garlic. It has the sp. gr. 0.874 at 40°, boils at 51°, is neutral, dissolves in 24 parts of water, does not precipitate nitrate of silver, and when kindled burns with a luminous flame edged with green, producing vapours of hydrochloric acid. Passed through a red-hot tube, it is resolved into equal volumes of hydrochloric acid and olefiant gases. Its vapour, mixed with chlorine, and first kept for 24 hours in the dark, then exposed to the sun-light, produces a series of compounds in which hydrogen is gradually replaced by chlorine, till at last, all the hydrogen being removed, there is left chloride of carbon (C_4Cl_6) and hydrochloric acid. (Laurent.) If left long in contact with hydrated alkalies, it produces chloride of the metal, and hydrate of oxide of ethyle (alcohol).

Formula of the chloride of ethyle, C_4H_5Cl , or $AcCl$.

BROMIDE OF ETHYLE.

Syn. Hydrobromic Ether.—Discovered by Serullas. One part of bromine is dissolved in 4 of alcohol, and the solution being introduced into a tubulated retort, connected with a good cooling apparatus, a quantity of phosphorus, equal to $\frac{1}{8}$ of the weight of the bromine, is added. After the heat produced by the solution of the phosphorus has subsided, the liquid is distilled with a very gentle heat. Water added to the distilled liquid causes the bromide of ethyle to separate. It is a colourless and very volatile liquid, having a penetrating ethereal smell and taste; heavier than water, miscible with alcohol and

ether in every proportion. It is not decomposed by contact with water.

Formula, C_4H_5Br , or $AeBr$.

IODIDE OF ETHYLE.

Syn. Hydriodic Ether.—Discovered by Gay-Lussac. Obtained by saturating alcohol with hydriodic acid and distilling; or by the use of iodide of phosphorus, like the preceding substance.

It is a colourless liquid, of a penetrating ethereal smell, boiling alone at 160° ; but, when heated along with water, its temperature does not rise beyond 150° . Its density at 70° is 1.92. It takes fire with difficulty. Its vapour, passed through a red-hot tube, is resolved into charcoal, iodine, and a new substance which contains iodine and carbon, is not very volatile, and is insoluble in water, acids, and alkalies. This liquid has not yet been sufficiently examined.

Formula of iodide of ethyle, C_4H_5I , or AeI .

When the bromide and iodide of phosphorus are employed to produce the last two substances, the phosphorus is oxidized at the expense of the oxide of ethyle, while the ethyle combines with the bromine or iodine: 3 at. alcohol, and 1 at. sesquibromide of phosphorus, for example, yield 1 at. hydrated phosphorous acid, and 3 at. bromide of ethyle. $3AeO,HO + PBr_3 = 3AeBr + PO_3,3HO$.

SULPHURET OF ETHYLE.

Sulphuret of ethyle is obtained, according to Regnault, when chloride of ethyle is conducted in the gaseous form through a solution of proto-sulphuret of potassium in alcohol. After some time, chloride of potassium is separated, and the liquid contains sulphuret of ethyle, which may be precipitated by the addition of water. Sulphuret of ethyle has a disagreeable penetrating odour, similar to that of garlic: its specific gravity is 0.815; it boils at 153° . Its formula is $C_4H_5S = AeS$.

HYDROSULPHURET OF SULPHURET OF ETHYLE.

Syn. Mercaptan.—Discovered by Zeise. To prepare this remarkable compound, aqua potassæ of sp. gr. 1.28 is first saturated with sulphuretted hydrogen gas, and thereby converted into a strong solution of hydrosulphuret of sulphuret of potassium. It is then distilled along with an equal volume of a solution, of the same density, of the double sulphate of oxide of ethyle and lime (sulphovinate of lime). The

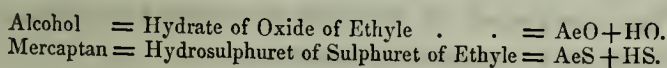
operation is performed in the water-bath, and the receiver is carefully cooled. The distilled liquid is purified from any free sulphuretted hydrogen that may be present by digestion and rectification with a little red oxide of mercury, and from water and alcohol by digestion with chloride of calcium.

Mercaptan is formed also, according to Regnault, when chloride of ethyle and a solution in alcohol of the combination of sulphuret of potassium with sulphuretted hydrogen are brought together.

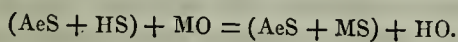
Mercaptan is a clear, colourless, mobile, ethereal liquid, possessing a very strong penetrating disagreeable odour, resembling that of garlic or assafœtida. It boils at about 98° (according to Zeise, at 144°); has the sp. gr. 0.842 at 60° ; is very inflammable, burning with a blue flame, and is neutral to test paper. It is sparingly soluble in water, miscible with alcohol and ether in all proportions. At a very low temperature it congeals into a foliated crystalline mass. It dissolves sulphur, phosphorus, and iodine.

Its empirical formula is $C_4H_6S_2 = AeS + HS$.

The chemical relations of mercaptan correspond to its constitution. It is alcohol, in which the oxygen has been replaced by sulphur; or it is the compound of ethyle with sulphur, corresponding to alcohol, in which ethyle is combined with oxygen. Thus:—



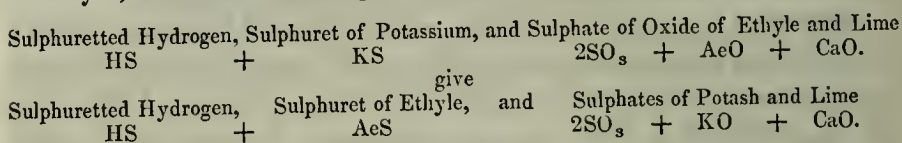
As water, in the hydrates of bases, for example,—in alcohol,—acts the part of a weak acid, so does the sulphuretted hydrogen (hydrosulphuric acid) in mercaptan; and, in many compounds derived from it, the hydrogen of the sulphuretted hydrogen is replaced by a metal, producing a metallic sulphuret, which combines with the sulphuret of ethyle. This happens when metallic oxides are placed in contact with mercaptan, when the hydrogen of the sulphuretted hydrogen and the metal of the oxide exchange places.



Where the metal forms with sulphur a highly negative sulphuret, the resulting compound with the positive or basic sulphuret of ethyle is permanent and not easily decomposed; as in the cases of lead, copper, silver, gold, and mercury. But where the resulting sulphuret is more positive or basic, its affinity with the sulphuret of ethyle is weak, and the compound is unstable, as in the case of potassium or sodium. Hence the hydrates of potash and soda hardly act perceptibly on mercaptan, while the oxides of gold and mercury are acted on by that substance energetically, with disengagement of heat, and formation of

stable, well-defined, crystalline compounds. Most of these are decomposed by sulphuretted hydrogen, which, being the strongest sulphur acid, expels the metallic sulphuret, taking its place, and reproducing mercaptan.

In the production of mercaptan, the sulphate of oxide of ethyle and of lime acts on the hydrosulphuret of sulphuret of potassium, producing sulphate of potash, sulphate of lime, and hydrosulphuret of sulphuret of ethyle, as in the following scheme:—



COMPOUNDS OF SULPHURET OF ETHYLE.

These compounds are commonly produced by the direct action of the aqueous or alcoholic solution of mercaptan on the metallic oxides, chlorides, or salts. The nature of the reaction has been already explained. In the case of potassium and sodium, the compounds can only be formed by the action of these metals on mercaptan; in this case hydrogen gas is evolved, and white crystalline compounds of sulphuret of ethyle with the sulphurets of potassium and sodium are produced. These compounds are instantly decomposed by water, producing potash or soda, and reproducing mercaptan.

The compounds of sulphuret of ethyle with the sulphurets of lead, copper, mercury, and gold, resist the action of alkalies, and of most acids: they are insoluble in water.

Sulphuret of Lead and Ethyle. Mercaptide of Lead.—Formula, $\text{AeS} + \text{PbS}$. Lemon-yellow needles and scales.

Sulphuret of Mercury and Ethyle. Mercaptide of Mercury.—Formula, $\text{AeS} + \text{HgS}$. It forms a white crystalline pearly mass, unctuous to the touch, fusible at 188° , soluble in boiling alcohol, from which it crystallizes on cooling. By a strong heat it is decomposed; producing cinnabar, metallic mercury, and a colourless volatile liquid, not yet examined.

Sulphuret of Gold and Ethyle. Mercaptide of Gold.—Forms a colourless, thick, gelatinous precipitate. When distilled it yields a colourless liquid, not examined, depositing a little sulphur and metallic gold.

BISULPHURET OF ETHYLE.

Discovered by Morin. This compound is obtained when two parts of sulphuret of potassium and three parts of the double sulphate of

ethyle and potash are subjected to distillation with an equal weight of water. The ethereal liquid which is the product of the distillation is a mixture of several compounds, one of which is the bisulphuret of ethyle. It boils at 304° F., is colourless, and of an extremely disagreeable smell. Its formula is $C_4H_5S_2 = AeS_2$. The mixture obtained by the distillation has received the name of Thialic oil.

SULPHOETHYLIC ACID.

When mercaptan is heated gently with nitric acid, 1 eq. of hydrogen is oxidized, and a new acid is formed, discovered by Löwig, which contains the elements of sulphuric acid and of sulphuret of ethyle, $AeS + SO_3 = C_4H_5S_2O_3$. It forms with bases easily crystallizable salts, which are very soluble in water. During its formation, a certain quantity of mercaptan is entirely decomposed, and sulphuric acid produced, but this can be separated by saturating the liquid with baryta, which forms a soluble salt with sulphoethylic acid.

SELENIURET OF ETHYLE.

Is obtained, according to Löwig, by distilling seleniuret of potassium with sulphovinate of lime or potash.

Probable formula, $AeSe$, or $AeSe + HSe$.

CYANIDE OF ETHYLE.

Discovered by Pelouze. A dry mixture of equal parts of sulphovinate of potash and cyanide of potassium is subjected to distillation, and the product rectified along with chloride of calcium. It is a colourless liquid, of a penetrating garlic odour, boiling at 180° . Sp. gr. 0.700. Is decomposed by oxide of mercury, but not by the alkalies. It is highly poisonous, inflammable, miscible with alcohol and ether, sparingly dissolved by water. In its production, the oxide of ethyle in the sulphovinate, acting on the cyanide of potassium, produces potash, which unites with the sulphuric acid, and cyanide of ethyle, which distils over. Formula, $AeCy$.

SULPHOCYANIDE OF ETHYLE.

By the action of sulphocyanide of potassium on chloride of ethyle, this compound is formed. (Löwig.) It is purified by solution in ether, and separated from the ether by distillation. Its density and boil-

ing points are the same as those of water. It is a colourless liquid, of a sweetish taste, like that of aniseed, and a penetrating alliaceous smell. Formula, AeCyS_2 .

SALTS OF OXIDE OF ETHYLE.

Oxide of ethyle (ether) forms with acids neutral and acid salts. In regard to its power of neutralizing acids, it follows the general laws of the capacity of saturation of the acids. The neutral salts of oxide of ethyle have no action on vegetable blues. They differ from inorganic salts in this, that the acid or the oxide of ethyle are not replaced by other acids or metallic oxides, when their solutions are mixed with those of inorganic salts at the ordinary temperature. For example, oxalate of oxide of ethyle (oxalic ether) gives no precipitate of oxalate of lime with an alcoholic solution of chloride of calcium.

In contact with hydrated alkalies, they are decomposed; slowly at the ordinary temperature, rapidly if boiled. The alkali combines with the acid, while the oxide of ethyle and the hydratic water of the alkali combine in the nascent state, producing alcohol.

Many of these neutral salts are only half decomposed by alkalies and metallic oxides, so that double salts of oxide of ethyle and metallic oxides are formed. All such double salts hitherto known are soluble in water, and possess, in reference to the state of the oxide of ethyle contained in them, the same character as the neutral salts; so that the acids they contain cannot be precipitated by the usual reagents. In this they are analogous to the double salts which sesquioxide of chromium and some other bases form with oxalic acid, in which the oxalic acid cannot be detected by a salt of lime. The metallic oxide in these double salts of oxide of ethyle may be replaced by other metallic oxides, or removed by a stronger acid. In the latter case it is replaced by water, and the acid salts of oxide of ethyle (for example, sulphovinic, phosphovinic, or oxalovinic acids, as they are called) are produced.

These acid salts of ethyle possess, in the concentrated state, considerable stability, and may be heated to 212° without decomposition. Many of them, the acids of which form hydrates which are not volatile, are resolved by heat into ether, which distils off, and the acid, or rather its hydrate, which remains behind. If these acid salts of ethyle be much diluted, they are decomposed at the ordinary temperature, and still more rapidly if boiled; a hydrate of the acid is formed, and the oxide of ethyle combines with water, producing alcohol.

If a concentrated solution of the acid sulphate of oxide of ethyle be

heated with the hydrates of many other acids, it most commonly happens that these other acids unite with the oxide of ethyle to form neutral salts, while a hydrate of sulphuric acid is left. Thus mucic acid, oleic acid, stearic acid, &c., when heated with a mixture of sulphuric acid and alcohol, yield the mucate, oleate, and stearate of oxide of ethyle, &c.

When the concentrated acid salts of oxide of ethyle are distilled along with other salts, the acids of which are volatile, and form volatile compounds with oxide of ethyle, the acid of the acid salt of oxide of ethyle combines with the base of the other salt, and the oxide of ethyle distils over in combination with the volatile acid. In this way are the neutral salts of oxide of ethyle with all volatile acids prepared. Example: acid sulphate of oxide of ethyle (sulphovinic acid) distilled with acetate or formiate of potash, gives neutral acetate or formiate of oxide of ethyle, and bisulphate of potash.

The neutral double salts of oxide of ethyle, heated or distilled with many acids, are decomposed into an acid salt of a metallic base which remains behind, while the oxide of ethyle combines with the acid which was added. Example: sulphate of potash and oxide of ethyle (sulphovinate of potash), heated with hydrated acetic or œnanthic acid, yields acetate or œnanthate of oxide of ethyle, while bisulphate of potash is left.

Chloride of benzoyle, heated with alcohol, is resolved, at the expense of the water of the alcohol, into hydrochloric acid and benzoic acid. The latter combines, in the nascent state, with the oxide of ethyle, forming benzoate of oxide of ethyle (benzoic ether), which distils over.

OXIDE OF ETHYLE AND SULPHURIC ACID.

The neutral sulphate of oxide of ethyle is unknown. The acid sulphate, known under the names of sulphovinic and ethero-sulphuric acid, is obtained directly by bringing the vapour of ether into hydrated sulphuric acid, as long as it is absorbed. Water being added to the mixture, after some hours the uncombined ether is separated, but a great part remains combined with the sulphuric acid. It is, however, prepared most easily, and in largest quantity, by heating a mixture of hydrated sulphuric acid and alcohol.

The acid decomposes the alcohol, uniting with the ether; while the water, both of the alcohol and of the acid, combines with the acid sulphate of oxide of ethyle.

[As ether is obtained by distilling such a mixture, the effect of heat on it has been the subject of many laborious investigations, which have

led at different times to conflicting theories on the formation of ether. In the following pages will be found a collection of all the established facts connected with this very interesting subject, together with that view of the production of ether which appears most consistent with those facts. We are indebted for it to Liebig, whose researches on this subject have powerfully contributed to dissipate the obscurity in which it was so long enveloped.—Editor.]

a. It has been observed that hydrated sulphuric acid, containing as much as 55 p. c. of water, (1 at. anhydrous acid and 4 at. water,) does not decompose alcohol at the ordinary temperature, but that at the boiling temperature it does so, producing the acid sulphate of oxide of ethyle.

b. It has further been proved, that, by cooling this mixture, the proportion of acid sulphate of ethyle again diminishes, and that by diluting it with water the acid sulphate undergoes a further decomposition.

c. In this case the oxide of ethyle separates from the acid, and unites with water, reproducing alcohol.

d. A mixture of 9 parts of oil of vitriol ($\text{SO}_3 + \text{HO}$) with 5 parts of alcohol at 85 per cent., after having been heated to its boiling point, contains exactly the elements of 2 at. anhydrous acid and 1 at. ether, or 1 at. anhydrous bisulphate of oxide of ethyle, with 4 at. water.

According to the common opinion, the 2 at. of sulphuric acid act on 1 at. alcohol, so that only half of the acid combines with ether; thus producing, on the one hand, anhydrous bisulphate of ethyle, and on the other a diluted hydrated acid with 4 atoms of water, while one-half of the alcohol remains uncombined in the solution. Both suppositions are totally without foundation.

e. It is obvious, that, if the bisulphate of oxide of ethyle has a composition analogous to that of the double salts of that base, it must contain, along with the oxide of ethyle, a certain quantity of water replacing the metallic oxide in the double salt. There is besides reason to believe, from the phenomena of the distillation of ether, that the bisulphate of oxide of ethyle has as strong an affinity for water as the sulphuric acid which it contains. But in this case the mixture must contain an acid with less than 4 atoms of water; which, as we have seen (*a*), cannot exist along with free alcohol, without decomposing it, and producing bisulphate of oxide of ethyle.

f. A mixture of 100 parts oil of vitriol, 48 parts alcohol, and $18\frac{1}{2}$ parts water, (2 at. sulphuric acid, 1 at. ether, and 6 at. water,) boils at 284° . Now, if only half the sulphuric acid is present in the state of bisulphate of oxide of ethyle (anhydrous), then there must

also be present, along with the free alcohol, a hydrated acid with 6 at. water. But acid of this strength boils at 222° .

g. When dry chlorine gas is passed through both the mixtures above mentioned, no hydrochloric acid is formed. Now, since free alcohol boils at 173° , and is instantly decomposed by chlorine, with the production of hydrochloric acid, and other compounds containing chlorine, while the bisulphate of oxide of ethyle, on the contrary, is not altered by chlorine, the above facts show that the mixture contains no free alcohol. Further, since the oxide of ethyle and sulphuric acid in the mixture are present in the proportions in which they exist in the bisulphate of oxide of ethyle, it follows that the mixture can contain no free acid, and must, therefore, be considered as a compound of bisulphate of oxide of ethyle with water.

h. When the mixture is heated beyond 284° , the bisulphate of oxide of ethyle is decomposed into ether and water, which distil over. An effervescence, similar to brisk ebullition, takes place, because the ether at that temperature assumes the form of gas. If oil of vitriol be added, the temperature must be raised to from 300° to 330° before this decomposition occurs; and with a great excess of sulphuric acid the mixture blackens, yielding only traces of ether, while the greater part of it is resolved into new products.

i. If alcohol be added to the original mixture, the alcohol passes over anhydrous, till the temperature rises to 258° or 260° , when traces of ether appear. At this temperature, therefore, the decomposition of the bisulphate of oxide of ethyle begins, when an excess of alcohol is present. If so much water is added as to keep its boiling point below 258° , alcohol alone, without ether, distils over.

k. If a current of dry air be made to pass through the mixture while heated to 284° , the boiling point sinks to 270° , and this reduction of temperature causes the production of ether to cease, alcohol alone passing over.

All these phenomena are explained by the following considerations:—

l. At temperatures above 284° , the bisulphate of oxide of ethyle is decomposed into ether which separates as gas, and sulphuric acid which mixes with the undecomposed portion.

m. If we consider each particle of the bisulphate of oxide of ethyle as composed of ether, anhydrous sulphuric acid, and water, it is clear that the anhydrous acid, at the moment of its separation from the ether, must seize on all water, free or combined, in the vicinity of the ether.

n. Thus, at the moment the ether becomes free, the anhydrous acid,

also set free, prevents it from uniting with water to form alcohol. But when the gaseous ether passes through the undecomposed hydrated bisulphate of oxide of ethyle, a certain proportion of the water of that compound must evaporate in the dry gas, and in these circumstances the ether and water do not combine together.

The surface of the effervescing liquid has the temperature at which bisulphate of oxide of ethyle is decomposed, but at this temperature, 284° , the water of that compound is gaseous. There are thus produced, simultaneously, water in the gaseous form by evaporation, and ether, also gaseous, by decomposition; which, as both are in the nascent state, unite to form alcohol.

Thus the alcohol, always observed to distil over with the ether, is derived from the surface; the ether and water, which distil over, proceed from the decomposition in the interior of the liquid. This explains why no ether is obtained when the liquid is not in brisk ebullition, no matter how high the temperature may be; it explains further why more alcohol is obtained when a current of dry air passes through the liquid, since in that case the same decomposition goes on in the interior of the liquid as generally occurs at the surface.

In proportion as the quantity of water in the bisulphate of oxide of ethyle is increased, the tension, that is, the quantity of water evaporating at a given temperature, increases also. A solution of the bisulphate, containing 4 atoms of water, must give off at 284° less water than one containing 5 or 6 atoms of water. This consideration explains the following phenomena:—

When the above-mentioned mixture, consisting of 2 at. anhydrous acid, 1 at. ether, and 4 at. water, is distilled, ether, alcohol, and water pass over at 284° ; and the first portion contains 19 of water to 100 of ether. Its sp. gr. is 0.758. There has, therefore, distilled less water than the proportion necessary to form alcohol with the ether, namely, 22.36 of water to 100 of ether. If the mixture distilled contain 2 at. anhydrous acid, 1 at. ether, and 5 at. water = 100 parts acid, 48 alcohol, and $18\frac{1}{2}$ water, the product of the distillation has the sp. g. 0.778, and contains 21.43 of water to 100 of ether. With a mixture of 2 at. acid, 1 at. ether, and 6 at. water = 100 parts acid, 48 alcohol, and 27 water, the product contains 22 of water to 100 of ether, and has the sp. gr. 0.796 to 0.798. But this is as nearly as possible the sp. gr. of alcohol. When, therefore, in this mixture there are 3 atoms of water for 1 of acid, the gaseous ether carries off its own volume of the vapour of water.

If we imagine, in this last mixture, one half of the bisulphate of oxide of ethyle decomposed, it will then contain—

1 at. dry Acid	} combined as Bisulphate of Ethyle.
$\frac{1}{2}$ at. Ether	
1 at. free Acid,	
$5\frac{1}{2}$ at. Water.	

If we now add $\frac{1}{2}$ at. alcohol, the free acid will decompose this alcohol, and we shall have the original mixture of 2 at. dry acid, 1 at. ether, and 6 at. water. This mixture yields ether and water in the proportions to form alcohol. It is obvious that the proportions are in no way altered if alcohol is merely added in volume exactly equal to the liquid distilled off, which contains the elements of alcohol. In this case the acid retains its power to cause alcohol to be resolved into ether and water to infinity. But, in preparing ether, pure alcohol is not used, only spirit of from 85 to 90 per cent.; so that with every drop of alcohol which is added there is introduced more water than corresponds to the above proportion (1 at. acid to 3 water).

Now it has been mentioned, that sulphuric acid, combined with 4 at. water, is still capable, with the aid of heat, of converting alcohol into bisulphate of oxide of ethyle. In this case, 2 at. acid take up 1 at. ether, and the resulting bisulphate contains 9 at. water, namely, 8 from the acid, and 1 from the ether. But such a mixture, which boils at 258° , produces alcohol alone, not ether.

An acid containing $4\frac{1}{2}$ at. water boils alone at 258° , namely, at the point where the decomposition of the bisulphate of ethyle begins. It is therefore clear, that, when this diluted acid, combined with ether, is made to boil, water is produced simultaneously with ether at all points where the latter is formed. But when water and ether meet in the nascent state, they unite to form alcohol. Hence the proportion of 9 at. water to 2 of dry acid is the limit of the dilution of the bisulphate, beyond which boiling produces no ether. When ether, therefore, is prepared from alcohol which is not anhydrous, we shall obtain ether, until, by the addition of water introduced with the alcohol, a mixture is formed containing $4\frac{1}{2}$ at. water to 1 at. dry acid.

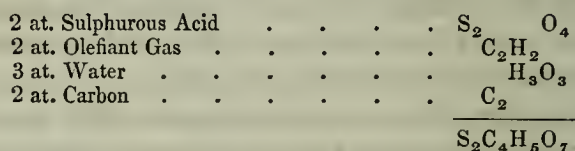
Experience has shewn that when a mixture of 9 parts oil of vitriol and 5 parts alcohol at 90 p. e. is employed, the production of ether ceases when 31 parts of such alcohol have been added. If more be added, alcohol alone distils over, with a mere trace of ether.

Supposing the whole water of this spirit to remain behind, while the elements of pure alcohol, in the form of ether and water, distil over, the residue contains at this point rather more than 3 at. water to 1 at. dry acid. But since, in the beginning of the distillation, more ether, or less water, passed over than the proportion necessary to produce alcohol, we may consider, without risk of error, $3\frac{1}{2}$ to 4 at. water to 1 at. dry acid as the limit fixed by experience for the productive

preparation of ether. From this point, when alcohol not anhydrous is added, as the liquids cannot instantly mix, there is produced, at some points, a mixture containing $4\frac{1}{2}$ at. water to 1 at. dry acid, which, as we have shewn, yields no ether when boiled.

The addition of an excess of sulphuric acid to the mixture prevents the decomposition of the bisulphate of oxide of ethyle, till the temperature rises so high that new reactions take place between the elements of the oxide of ethyle and the sulphuric acid. This happens at about 320° . The principal products of this reaction are, sulphurous acid, olefiant gas, water, and carbon. In certain proportions, acetic acid is formed. With a great excess of acid, traces of formic acid and carbonic oxide are produced. As long as olefiant gas comes off, carbonic acid cannot be detected. During this decomposition, sulphurous acid and olefiant gas are given off in equal volumes, which sufficiently explains the reaction.

The elements of 1 atom bisulphate of oxide of ethyle arrange themselves as follows :—



Carbon and water are the elements of acetic acid, the formation of which must diminish the quantity of carbon in the residue. By the action of the sulphuric acid in excess on acetic acid, formic acid and sulphurous acid are formed; and by the action of the sulphuric acid in excess on formic acid, carbonic oxide gas is produced.

It is probable that, in this decomposition, the elements of sulphuric acid and ether first arrange themselves so as to form ethionic or isethionic acids, and that the above-named products are derived from the further decomposition of these acids. At least, Ettling found in the residue an acid agreeing in many of its properties with isethionic acid. But the formation of these substances would not alter the proportions of the ultimate products.

The sulphate of oxide of ethyle and etherole (sweet oil of wine) is produced in small quantity. This is easily explained, as the composition of that body represents neutral sulphate of ethyle—1 at. of water. The carbon of the residue, when washed and dried, forms a black powder, soiling paper or the finger strongly. If heated, it yields first water, then sulphur. The sulphur it contains cannot be extracted from it by alkalis or sulphuret of carbon.

The purest bisulphate of oxide of ethyle is obtained when the sul-

phate of oxide of ethyle and etherole (sweet oil of wine) is gently heated with 4 parts of water. It is decomposed; etherole, in the form of a yellow oil, separating, while bisulphate of oxide of ethyle is dissolved by the water. By adding sulphuric acid to a solution of the sulphate of baryta and oxide of ethyle till all the baryta is precipitated, or by decomposing the sulphate of lead and oxide of ethyle by sulphuretted hydrogen, the bisulphate may also be prepared.

It forms with water a very sour liquid. It cannot be evaporated, when diluted, without decomposition. With bases it forms a series of double salts. Formula, $\text{AeO}, \text{SO}_3 + \text{HO}, \text{SO}_3$.

DOUBLE SALTS OF THE SULPHATE OF OXIDE OF ETHYLE.

When the bisulphate of oxide of ethyle is neutralized by bases, double salts are formed, containing 2 at. sulphuric acid, 1 at. oxide of ethyle, and 1 at. of the base which is added. They are, without exception, soluble in water and hydrous alcohol, whence it happens that the sulphuric acid they contain is not detected by the usual reagents. But if to a solution of one of these double salts hydrochloric acid be added, and the mixture heated to boiling, alcohol is expelled with the vapour of water, and in the residual liquid the sulphuric acid can now be recognized. When exposed to heat, they are decomposed, and, according to the temperature, they yield sulphate of oxide of ethyle and etherole, with alcohol, sulphurous acid, olefiant gas, and in the residue a sulphate mixed with carbon. Distilled with quicklime at a temperature not higher than 300° , they are entirely converted into sulphates and the two first-mentioned products. The double salt of baryta, distilled with a diluted sulphuric acid containing 4 at. water, yields a mixture of ether and alcohol. Most of them contain water of crystallization, which they part with entirely in vacuo over sulphuric acid at the ordinary temperature. The double salt of potash alone crystallizes without water. When boiled in the form of concentrated solution in water, they are decomposed, although slowly. Bisulphates, or mixtures of sulphuric acid and neutral sulphates, are left, while alcohol passes over. Heated in the dry state, with hydrate of baryta or of lime, these salts are resolved into fixed neutral sulphates and alcohol. Chlorine gas, passed through their solutions, does not decompose the oxide of ethyle, nor set sulphuric acid free. When supersaturated with potash, the salts of potash and soda may be boiled and evaporated without decomposition. If the dry salts are melted with the hydrated alkalis, the oxide of ethyle is destroyed, and all the sulphuric acid remains combined with the alkali.

To prepare these salts, a boiling hot mixture of equal parts of oil of vitriol and alcohol of 85 p. c. is saturated with milk of lime, carbonate of baryta, or carbonate of lead, when a soluble double sulphate of oxide of ethyle with lime, baryta, or oxide of lead, is formed, and separated by filtration from the insoluble sulphates of those bases. If one of these salts be mixed with carbonate of potash, soda, or ammonia, the insoluble carbonate is precipitated, and the filtered liquid contains the double salt of oxide of ethyle with the alkaline base. Or the free bisulphate of oxide of ethyle is saturated with a base; or, lastly, the double salt of baryta is precipitated by a soluble sulphate. In this last way are prepared the double salts of oxide of ethyle with magnesia, oxide of manganese, &c. As the other properties of these salts offer no peculiar interest, it is unnecessary to detail them.

General formula for these double salts, $\text{AeO},\text{SO}_3 + \text{MO},\text{SO}_3 + \text{aq.}$ They are often described under the name of sulphovicates or ethero-sulphates.

Sulphate of Oxide of Ethyle and Potash.—Formula, $\text{AeO},\text{SO}_3 + \text{KO},\text{SO}_3$ (Marchand.) Forms transparent and colourless scales, like chlorate of potash, permanent in the air, soluble in its own weight of water, of a sweetish saline taste, soluble in spirit of wine, insoluble in absolute alcohol and ether. When heated beyond 212° , it is decomposed without undergoing fusion.

Sulphate of Oxide of Ethyle and Baryta.—Formula, $\text{AeO},\text{SO}_3 + \text{BaO},\text{SO}_3 + 2 \text{ aq.}$ (Marchand.) Brilliant transparent tables, permanent in the air, or rhombic prisms, of a sharp saline taste, soluble in their own weight of water, insoluble in cold, sparingly soluble in hot anhydrous alcohol. It loses half of its water by boiling with alcohol, and the whole of it in a current of air at 112° , or in vacuo at the ordinary temperature. The hydrous salt is decomposed at 212° , the anhydrous is not.

Sulphate of Oxide of Ethyle and Lime.—Formula, $\text{AeO},\text{SO}_3 + \text{CaO},\text{SO}_3 + 2 \text{ aq.}$ (Serullas, Marchand.) Large, thin, six-sided plates; 4 parts of water at 65° dissolve 5 parts of salt. It is soluble in absolute alcohol with the aid of heat. When distilled, it yields besides the usual products, according to Marchand, a peculiar volatile liquid, in very minute quantity, which is miscible with water, alcohol, and ether.

Sulphate of Oxides of Ethyle and Lead.—1. Neutral. Formula, $\text{AeO},\text{SO}_3 + \text{PbO},\text{SO}_3 + 2 \text{ aq.}$ (Dumas, Marchand.) Large colourless transparent tables, very soluble in water and alcohol, reddening litmus. Gradually undergoes spontaneous decomposition, exhales ether, and becomes unctuous from sulphate of oxide of ethyle and etherole.—2. Basic. Formula, $\text{AeO},2\text{PbO},2\text{SO}_3$. Formed by di-

gesting the neutral salt with oxide of lead. It is an uncrystallized white mass, very soluble in water and alcohol, not changing vegetable blues. It yields, when distilled, alcohol and sulphate of oxide of ethyle and etherole, without any other volatile products.

OXIDE OF ETHYLE AND PHOSPHORIC ACID.

Acid Phosphate of Oxide of Ethyle. Syn. Phosphorvinic Acid; Etherophosphoric Acid.—When hydrated phosphoric acid, $\text{PO}_5 + 3\text{HO}$, is mixed with alcohol, much heat is developed. Of the three atoms of basic water which the acid contains, one is replaced by oxide of ethyle, producing an acid salt with 3 atoms of base, analogous to the common phosphates. If the acid be diluted with so much water as to have the sp. gr. 1.2, it no longer decomposes alcohol. (Pelouze.)

It is obtained pure by decomposing the phosphate of baryta and oxide of ethyle by sulphuric acid: 100 parts of the crystallized salt require 25.33 sulphuric acid (oil of vitriol). The sulphate of baryta being separated by the filter, the solution is evaporated, first in the water-bath, afterwards in vacuo over sulphuric acid. (Pelouze.)

It forms a syrupy, colourless, very acid liquid, miscible with water, alcohol, and ether. It may be boiled in the diluted state without decomposition. The concentrated acid at a high temperature is decomposed, with disengagement of ether, alcohol, and inflammable gases, and deposition of carbon. It coagulates albumen. In the most concentrated state it shows a tendency to crystallize. Formula, $\text{PO}_5 + \text{AeO} + 2\text{HO}$.

PHOSPHATE OF OXIDE OF ETHYLE WITH METALLIC OXIDES.

If the acid phosphate of oxide of ethyle be brought in contact with metallic oxides, the two atoms of basic water contained in it are separated, and replaced by their equivalent of metallic oxide; and salts with 3 atoms of base are formed, according to the general formula, $\text{PO}_5 + \left\{ \begin{array}{l} \text{AeO} \\ 2\text{MO} \end{array} \right\}$. MO here is a metallic protoxide. Compounds of pyrophosphoric or metaphosphoric acids with oxide of ethyle have not yet been formed.

The phosphates of oxide of ethyle and other bases may be formed either by neutralizing the acid phosphate directly by the metallic oxide, or by precipitating the phosphate of oxide of ethyle and baryta with soluble carbonates or sulphates.

Phosphate of Oxide of Ethyle and Baryta. Syn. Phosphovinate or Etherophosphate of Baryta.—Formula, $\text{PO}_5 + 2\text{BaO} + \text{AeO} + 12 \text{ aq.}$ Phosphoric acid, evaporated to the consistence of thick syrup, is mixed with its own weight of pure alcohol or spirit of wine at 92 p. c., the mixture heated to the boiling point, and, after twenty-four hours, diluted with water, and neutralized with carbonate of baryta at the ordinary temperature. The solution is filtered from the precipitated phosphate of baryta, and evaporated at 100° till it crystallizes. It forms colourless, pearly, six-sided tables, soluble in 11 parts of water at 100° , in 15 parts at 68° , in 30 parts at 32° , and in 36 parts at 212° . A solution saturated at 100° becomes thick when heated to the boiling point, from the deposition of the hydrous salt. The water amounts to 29.1 p. c. At 302° it is entirely expelled. (Pelouze.)

OXIDE OF ETHYLE AND ARSENIC ACID.

According to D'Arcet, concentrated arsenic acid, when heated with alcohol, forms an acid salt, differing in its constitution from the acid phosphate. The acid arseniate of oxide of ethyle contains 3 atoms of base, namely 2 at. oxide of ethyle and 1 at. water, which last may be replaced by metallic oxides. Its formula is $\text{AsO}_5, 2\text{AcO}, \text{HO}$; and the general formula for its double salts is $\text{AsO}_5, 2\text{AeO}, \text{MO}$. These statements require confirmation.

OXIDE OF ETHYLE AND NITRIC ACID.

It was long supposed that nitric acid destroyed alcohol, and could not be made to enter into combination with oxide of ethyle; but it has now been ascertained that it is nitrous acid which destroys the alcohol, and as there is generally some nitrous acid present in the nitric acid, the products of its action produce more nitrous acid by deoxidizing the nitric acid, and thus the whole alcohol is decomposed. If, however, a little urea be added to the mixture of acid and alcohol, the nitrous acid is entirely decomposed, and the nitric acid then combines with the oxide of ethyle. When two ounces by measure of alcohol, and one ounce of pure nitric acid are employed, 20 grains of urea are found sufficient to prevent the appearance of nitrous acid; the action is moderate, and after a time the nitrate of oxide of ethyle begins to appear as a heavy oily liquid, the quantity of which is increased by the addition of water. When pure it is colourless; its sp. gr. is 1.112, and it boils at 185° . It is inflammable, burning with a white flame. It has a sweet taste and a pleasant smell, and

dissolves readily in alcohol, but very sparingly in water. Its formula is $C_4H_5O + NO_5 = AeO, NO_5$, and by digestion with an alcoholic solution of potash, it yields alcohol and nitrate of potash.

OXIDE OF ETHYLE AND HYPONITROUS ACID.

Hyponitrite of Oxide of Ethyle. Syn. Nitrous Ether; Hypo-nitrous Ether.—To prepare this compound in a state of purity, the following process has lately been given by Liebig. One part of starch, and 10 parts of nitric acid, sp. gr. 1.3, are introduced into a capacious retort, which is connected by means of a wide tube, bent at right angles, with a two-necked bottle, so that the further end of the tube reaches to the bottom of the bottle. Into this bottle is introduced a mixture of 2 parts of alcohol at 85 p. c. and 1 part of water, and it is surrounded by cold water. The second aperture of the bottle is connected, by means of a long and wide tube, with a good cooling apparatus, or condenser. The starch and nitric acid are heated in the water-bath; pure hyponitrous acid is disengaged, which, passing through the alcohol, instantly combines with the ether, forming hyponitrite of oxide of ethyle, which distils in a continuous stream. This process is very productive. By means of water, the new ether is purified from alcohol, and by standing over chloride of calcium, it is freed from water. The tube which connects the retort with the two-necked bottle must have a length of 2 or 3 feet, and must be surrounded with moist paper during the operation. If the alcohol be not carefully cooled, it becomes spontaneously hot and boils violently. From this moment the hyponitrite of ethyle is no longer pure.

The following methods, which are commonly given, yield a product contaminated by aldehyde in variable quantity. 2. Two parts of alcohol of 85 p. c. are mixed with 2 parts of nitric acid of sp. gr. 1.284, and the mixture is gently heated in a retort connected with a condenser surrounded with ice. The mixture quickly boils, and the fire is instantly removed. When no more passes over, the ethereal compound is purified by rectification at a very gentle heat. 3. In a strong cylindrical vessel are placed 9 parts of alcohol at 85 p. c. By means of a funnel tube ending in a narrow aperture, 4 parts of water are introduced below the alcohol, taking care that they do not mix. In the same manner 8 parts of fuming nitric acid are added under the water, so that the bottle contains three strata of liquid. It must be filled to four-fifths; and, in order that the stratum of water may be deep enough, the bottle should be three times as high as it is wide. It is now lightly stopped, and left to itself in a temperature not higher than 53°. After

two or three days, there are found in the bottle two strata, the uppermost of which is the ether, to be purified by rectification.

The hyponitrite of oxide of ethyle prepared by process 1 is pale yellow, has a most fragrant smell of apples and Hungary wines, boils at 62° , and has the sp. gr. 0.947 at 60° . It may be mixed with an alcoholic solution of potash without becoming brown; hyponitrite of potash and alcohol are formed. That made by processes 2 and 3 boils at 70° , has the sp. gr. 0.886 at 40° . Its smell is like that of the former, but at the same time suffocating. Mixed with an alcoholic solution of potash, it becomes dark brown, with production of resin of aldehyde. It is highly combustible, burning with a white flame. The ether of processes 2 and 3, when kept, becomes acid, while nitric oxide gas is given off. Hence it often bursts the bottles. It must, therefore, and on account of its great volatility, be kept in half ounce or ounce bottles very strongly made, in a cool place. This tendency to become acid is greater when air is admitted, and depends on the presence of aldehyde, which is oxidized by the oxygen of the air, or by the hyponitrous acid. If the liquid is allowed to remain in contact with milk of lime or aqua potassæ, the aldehyde is converted into resin of aldehyde; and the liquid is found to contain nitrate and hyponitrite of lime, with another salt of lime, not examined. By allowing the hyponitrite of oxide of ethyle to stand over dry nitrate of lime, and rectifying it along with that salt, it is rendered pure from alcohol and water. It is soluble in 48 parts of water, and miscible in all proportions with ether and alcohol.

Formula, AcO, NO_3 .

The spiritus ætheris nitrosi, or sweet spirit of nitre of the pharmacopœia, is a mixture of nitrous ether (the impure hyponitrite of oxide of ethyle above described) with rectified spirit of wine. It may be made by directly mixing these liquids, or by distilling nitric acid with a much larger proportion of alcohol than in the preceding processes. For example, 1 part of diluted nitric acid may be distilled with 6 parts of alcohol at 85 or 90 p. c., and 5 parts of distilled product drawn off. Its properties for the most part coincide with those of nitrous ether, but its sp. gr. is 0.825. It ought to be neutral; but must be carefully preserved in small bottles from the contact of air, as it otherwise gradually becomes acid. It is employed as a refrigerant and diuretic.

OXIDE OF ETHYLE WITH CARBONIC ACID.

The only compound under this head which has yet been obtained directly is the double carbonate of oxide of ethyle and potash. But

the neutral carbonate of oxide of ethyle (carbonic ether) has been formed indirectly by the action of potassium or sodium on neutral oxalate of oxide of ethyle (oxalic ether); a reaction which has not yet been fully explained.

Carbonate of Oxide of Ethyle and Potash. *Syn. Carbovinat of Potash.*—Formula, $\text{AeO}, \text{CO}_2 + \text{KO}, \text{CO}_2$. Discovered by Dumas and Peligot. Hydrate of potash, fused at a red heat, is dissolved in alcohol, and the solution is saturated with dry carbonic acid gas. The liquid congeals to a white paste, which contains the new double salt along with neutral carbonate and bicarbonate of potash. The mass is placed on a filter, and washed with pure ether; it is then covered with absolute alcohol, which dissolves the double salt alone. This solution, when mixed with ether, deposits the salt in crystals, which are collected on a filter, carefully pressed in bibulous paper, and dried in vacuo over sulphuric acid.

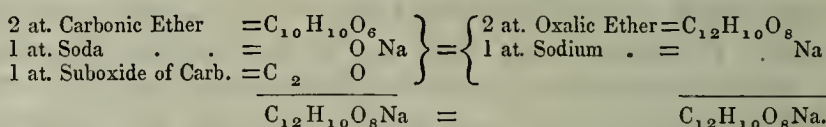
It forms pearly soft scales, unctuous to the touch, which, when distilled, yield carbonic acid, an ethereal liquid, an inflammable gas, and a residue composed of carbon and carbonate of potash. When placed in contact with water, this salt is instantly resolved into alcohol and bicarbonate of potash.

With ammonia and alcohol, carbonic acid forms a similar salt, which, however, cannot be separated in the same way from the carbonates of ammonia formed along with it.

CARBONATE OF OXIDE OF ETHYLE.

Syn. Carbonic Ether.—Formula, AeO, CO_2 . Discovered by Ettling. Fragments of potassium or sodium are gradually added to warm oxalic ether (p. 888), as long as gas is disengaged. The excess of metal being removed, the semi-solid mass produced is mixed with water and distilled, when the carbonic ether swims on the surface of the product of the distillation. Having separated it from the water, it is dried by contact with chloride of calcium, and rectified with potassium or sodium, till a portion, when acted on by caustic potash, yields no oxalate of potash. It forms a colourless, very fluid, ethereal liquid, possessing a burning taste and an aromatic ethereal odour, resembling that of oxalic ether. It is lighter than water, has the sp. gr. 0.975 at 66°, boils at 260°, is kindled with difficulty and burns with a blue flame. It may be mixed with alcohol and ether, but is insoluble in water. When mixed with an alcoholic solution of hydrates of potash or soda, it is quickly resolved into alcohol, and carbonate of potash or soda, which separate either as an oily concentrated solution in water, or as a crystalline

powder if no water be present. The formation of carbonic ether, which is attended by the production of several substances not yet examined, is as yet unexplained. According to Löwig's experiments, when sodium is made to act on oxalic ether, a suboxide of carbon, C_2O , and carbonic ether are produced.



A part of the carbonic ether is decomposed by sodium into carbonic oxide and soda-ether, AeO, NaO . When soda-ether comes in contact with water, alcohol and hydrate of the alkali are produced. The compound of the suboxide of carbon and soda is decomposed by water into formiate and nigrinate of soda. According to Löwig, nigrinic acid, $C_{14}H_7O_7$, is produced by the decomposition of oxalic ether by sodium. It has a brownish-red colour and a resinous appearance. It is formed by the suboxide of carbon, combining with the elements of water; $14(C_2O) + 8NaO + 14HO = 7(C_2HO_3, NaO) + C_{14}H_7O_7, NaO$.

OXIDE OF ETHYLE AND OXALIC ACID.

Oxalic acid forms with oxide of ethyle an acid salt and a neutral salt. The analysis of the latter by Dumas and Boullay first gave correct notions in regard to the composition of the so-called compound acid ethers.

Neutral Oxalate of Oxide of Ethyle. Syn. Oxalic Ether.—Discovered by Thenard. Formula, $AeO, \overline{Ox}$. To prepare it, 4 parts of binoxalate of potash are mixed in a retort with 5 parts of oil of vitriol and 4 of alcohol at 90 p. c., and distilled with a quick fire. As soon as the product is rendered turbid by the addition of water, the receiver is changed, and is no longer kept cool. The subsequent product is quickly mixed with 4 times its bulk of water, the ether which sinks to the bottom is separated, and agitated 4 or 5 times with new portions of water till it becomes neutral to test paper. The ether thus washed is introduced into a small dry retort, which must be filled up to nine-tenths of its capacity, and rectified. As soon as the product becomes clear, and the boiling goes on, not by jerks but smoothly, the receiver is changed. What now passes over is pure anhydrous oxalate of oxide of ethyle (oxalic ether).—(Ettling.)

It is a colourless, transparent, oily fluid, of sp. gr. 1.0929 at 46° , boiling at 370° , miscible with alcohol and ether, and having a peculiar aromatic smell. In a state of purity it may be kept many days under water, in which it is very sparingly soluble, without decomposition;

but when it contains but a trace of free acid or of alcohol, it is speedily resolved into oxalic acid, which is deposited in large transparent four-sided prisms, and alcohol. The same change occurs with an excess of fixed alkali.

DOUBLE SALTS OF OXALIC ACID WITH OXIDE OF ETHYLE AND METALLIC OXIDES.

When oxalic ether is dissolved in alcohol, and so much of a solution of fused potash or soda in alcohol is added as to neutralize one half of the oxalic acid, half of the oxide of ethyle separates, and combines with the water of the alkali to form alcohol. It is replaced by the alkali, and double salts are produced, containing 2 at. oxalic acid, 1 at. oxide of ethyle, and 1 at. potash or soda. When ammonia is added to oxalic ether, it is decomposed: with an excess of ammonia oxamide is produced: with less ammonia oxamethane is formed. Potassium and sodium decompose oxalic ether, producing carbonic ether and other products.

Binoxalate of Oxide of Ethyle. Syn. Oxalovinic Acid.—Formula, $\text{AeO}, \bar{\text{Ox}} + \text{HO}, \bar{\text{Ox}}$. Oxalate of ethyle and potash (see below) is dissolved in alcohol, and fluosilicic acid is added as long as it causes a precipitate. The filtered liquid contains the oxalovinic acid mixed with alcohol and water. It may be obtained free from alcohol by carefully adding sulphuric acid to the aqueous solution of the oxalate of ethyle and baryta (oxalovinate of baryta). It forms a very sour liquid, which is easily resolved, especially with the aid of heat, into oxalic acid and alcohol.

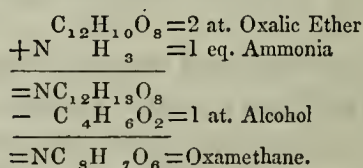
Oxalate of Oxide of Ethyle and Potash. Syn. Oxalovinate of Potash.—Formula, $\text{AeO}, \bar{\text{Ox}} + \text{KO}, \bar{\text{Ox}}$. One volume of oxalic ether is dissolved in 2 vols. alcohol; and after trying with a portion of this mixture how much of an alcoholic solution of potash is required to produce a slight alkaline reaction, rather less than half that proportion is added to the remaining mixture. If, for example, 10 fluid drachms of the mixture require 16 fluid drachms of an alcoholic solution of potash to neutralize the acid completely, producing a slight alkaline reaction, then to 100 volumes of the mixture, 75 volumes of the alcoholic solution should be added. The double salt, being insoluble in alcohol, separates. It is washed with alcohol, and dried in vacuo. It forms crystalline scales, anhydrous, and perfectly soluble in alcohol of 75 p. c. It is easily decomposed by acids and alkalies, but when dry it bears a heat of 212° without change.

Oxalate of Oxide of Ethyle and Baryta. Syn. Oxalovinate of Baryta.—Formula, $\text{AeO}, \bar{\text{O}}_x + \text{BaO}, \bar{\text{O}}_x$. When the oxalovinic acid is neutralized by carbonate of baryta, the liquid evaporated at the ordinary temperature, or in vacuo, yields this double salt. It crystallizes with difficulty, and is extremely soluble in water. By the addition of soluble sulphates to its solution, the corresponding double salts of other bases may be formed.

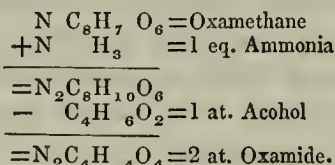
OXALATE OF ETHYLE WITH AMMONIA.

Oxamethane. Syn. Oxalate of Oxide of Ethyle and Oxamide; Oxamate of Oxide of Ethyle.—Formula, $\text{C}_8\text{H}_7\text{NO}_6$. Oxalic ether is dissolved in alcohol; and alcohol saturated with dry ammoniacal gas is added in small quantities, till a white powder begins to separate. After some hours the clear liquid is filtered from the precipitate, and evaporated, when oxamethane crystallizes, and may be purified by repeated solution and crystallization out of alcohol. It forms colourless transparent scales or plates, with a fatty lustre, melts at about 212° , distils unchanged at about 430° , is soluble in water and alcohol, neutral to test paper, and does not precipitate metallic salts. The aqueous solution, when boiled, is resolved into alcohol and binoxalate of ammonia. Mixed with excess of ammonia, it is instantly converted into oxamide and alcohol.

Explanation.—When to the elements of 2 at. oxalic ether are added those of 1 eq. ammonia, and from the whole are subtracted the elements of 1 at. alcohol, oxamethane is left.



When the oxamethane is again acted on by an excess of ammonia, the same decomposition is repeated. Alcohol is separated, and oxamide is formed.



These reactions are easily deduced from the constitution of ammonia and of oxalic acid. The former is $\text{NH}_2 + \text{H}$, the latter $2\text{CO} + \text{O}$. Oxalic ether in excess and ammonia yield oxamethane and alcohol, be-

cause 1 eq. hydrogen of the ammonia unites with 1 at. oxygen of the oxalic acid forming water, which with half the ether produces alcohol. The third atom of oxygen in the oxalic acid is replaced by amide (amidogen); thus, $2\text{CO} + \text{NH}_2$. This is oxamide, which unites with the half of the oxalic ether to form oxamethane. With an excess of ammonia this portion of oxalic ether undergoes the same decomposition.

Balard has recently shewn that oxamethane is a compound of oxide of ethyle with oxamic acid; but this does not affect the above explanation of its production and of its decomposition by excess of ammonia.

Berzelius considers the oxamic acid as oxalic acid, coupled with oxamide; and recent researches have shewn that there may exist a considerable number of similar acids in which known acids are coupled with their amides, as oxalic acid is here with oxamide.

BICARBOSULPHATE OF OXIDE OF ETHYLE.

XANTHIC ACID.

Syn. Bisulphocarbonate of Oxide of Ethyle.—Discovered by Zeise. Formula, $2\text{CS}_2 + \text{AeO}$. Is not known in the anhydrous state, but only in combination with water or metallic oxides.

Hydrated Xanthic Acid.—Formula, $\text{AeO}2\text{CS}_2 + \text{aq}$. Sulphocarbonate of oxide of ethyle and potash, (xanthate of potash, see p. 892,) in the dry state, is mixed with dilute sulphuric or hydrochloric acid. After some time a milky liquid is formed, from which, by the addition of more water, the new acid is deposited as a heavy oil, colourless or slightly yellow. It is to be quickly washed with water, and dried by standing over chloride of calcium.

It is an oily liquid, of a peculiar, strong, penetrating, and disagreeable odour, and a weak, acid, bitterish taste. It reddens litmus, but bleaches it after a time. It is very inflammable, burning with a blue flame, is spontaneously decomposed at temperatures above 75° , either alone or in contact with water, producing bisulphuret of carbon and alcohol. Under water containing absorbed oxygen or air, it becomes opaque and white, and is covered with a thick hard white crust. It decomposes alkaline carbonates with effervescence, the alkali replacing its basic water, and forming a double carbosulphate with the oxide of ethyle.

DOUBLE SALTS OF BISULPHURET OF CARBON WITH OXIDE OF ETHYLE AND METALLIC OXIDES.

These compounds, the xanthates of Zeise, are analogous in constitution to the preceding compound, Zeise's xanthic acid, the basic

water of the latter being replaced by its equivalent of the metallic oxide. The double salts of potash and soda are formed, when, to a solution of potash or soda in alcohol, bisulphuret of carbon is added as long as it is dissolved. The others are obtained by double decomposition. They are insoluble, and have generally a yellow colour; hence the name. When distilled, they yield volatile products, both liquid and gaseous; among which Zeise has noticed an amber-coloured oil, of peculiar properties, which he calls Xanthic oil.

The solutions of the soluble xanthates are decomposed by boiling; producing alcohol, bisulphuret of carbon, sulphuretted hydrogen, and a residue consisting of carbonate and hyposulphite of the metal, mixed with sulphur and sulphocarbonate (carbosulphate) of the metallic sulphuret.

These salts, dry or dissolved, may be preserved in close vessels; but they always exhale, when the bottle is opened, the peculiar smell of the bisulphocarbonate of oxide of ethyle (xanthic acid). The salts with alkaline and earthy bases are decomposed by acids which combine with the bases. The salts of lead and copper, on the contrary, resist the action of dilute acids, and are hardly decomposed, especially the lead salt, by sulphuretted hydrogen.

Bisulphocarbonate of Oxide of Ethyle and Potash. Syn. Xanthate of Potash.—Discovered by Zeise. Formula, $2\text{CS}_2, \text{AeO}, \text{KO}$. Formed, as above mentioned, by adding bisulphuret of carbon to a saturated solution of fused caustic potash in absolute alcohol, as long as it is dissolved.

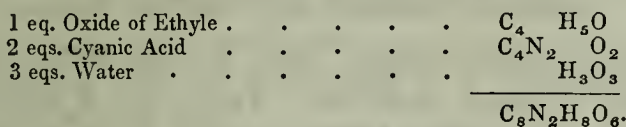
The liquid commonly becomes semi-solid when exposed to a cold of 32° , from the separation of fine crystals, which are collected on a filter, washed with ether, pressed in bibulous paper, and dried without access of air. Should no crystals appear, the solution must be concentrated by evaporation at a gentle heat, which is best done in a retort. The pure salt forms colourless or pale yellow anhydrous needles, soluble with a yellow colour in water, of a very bitter peculiar taste. It is soluble in alcohol, insoluble in ether: in a moist atmosphere it is converted into hyposulphite of potash.

Sulphocarbonate of Oxide of Ethyle and Suboxide of Copper. Syn. Xanthate of Copper.—When a solution of the preceding salt is mixed with that of a salt of oxide of copper, lemon-yellow flocculi of this double salt are obtained. The oxygen which the oxide of copper loses, in becoming suboxide, produces another compound, which adheres to the precipitate. According to Couerbe, it may be removed by ether; and, when pure, has the character of an oily liquid, solidifying at low temperatures. It appears to contain hydrogen and carbon in the same

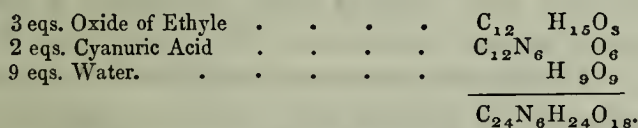
proportion as in olefant gas, but no sulphur. According to Zeise, the same body is left undissolved when the double salt of copper is dissolved in nitric acid.

ALLOPHANIC ACID.

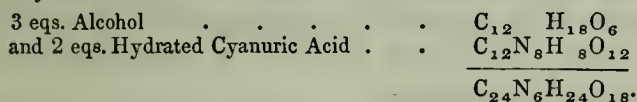
When the vapour of hydrated cyanic acid is brought in contact with alcohol, a number of hard brilliant colourless crystals are formed, the empirical formula of which is $C_8N_2H_8O_6$.* This may be interpreted as a compound of oxide of ethyle, cyanic acid, and water :



Or, trebling the formula, it becomes $C_{24}N_6H_{24}O_{18}$, and it may then be composed of



It was accordingly described by its discoverers, Liebig and Wöhler, as an anomalous cyanic or cyanuric ether, the latter formula being considered the more probable, because, when decomposed by heat, it yields alcohol and cyanuric acid. In fact, it contains the elements of



But Liebig and Wöhler, having observed not only the anomalous constitution of the compound considered as an ether, (since the ethers of oxygen acids contain no water, but only oxide of ethyle and the anhydrous acid, as, for example, acetic ether, $C_4H_5O + C_4H_3O_3$.) but also that, when acted on by baryta, it yielded alcohol and a salt which contained neither cyanic nor cyanuric acid, have lately studied the subject anew, and have found that this compound contains oxide of ethyle united to a new acid, *allophanic acid*, the formula of which is $C_4N_2H_3O_5$.

Allophanic acid is formed by the union of 2 eq. hydrated cyanic acid, $C_4N_2H_2O_4$, with 1 eq. of water derived from the alcohol, while

* In the *Annalen der Chemie und Pharmacie*, liv. 370, Liebig and Wöhler described a compound found in the mother-liquid of these crystals. It is very soluble in water, alcohol, and ether, and forms large tabular crystals, very fusible and volatile, the empirical formula of which is $C_6NH_7O_4$. This is exactly the composition of urethane or carbamate of oxide of ethyle (p. 896); and the properties of the two compounds are so similar, that it appears most probable they will be found to be identical. In the paper on allophanic acid (*Annalen*, lix. 291), Liebig and Wöhler do not allude to this compound.—W. G.

the oxide of ethyle thus produced combines with the new acid.
 $C_4H_5O, HO + 2(C_2NO, HO) = C_4H_5O, C_4N_2H_3O_5.$

Allophanic acid forms crystallizable salts with baryta, potash, soda, &c.; and when we attempt to isolate the acid from these salts by means of a stronger acid, it is immediately resolved, with the aid of 1 eq. of water, into carbonic acid and urea. $C_4N_2H_3O_5 + HO = 2CO_2 + C_2N_2H_4O_2.$ The same transformation occurs when the solutions of these salts are heated.

OXIDE OF ETHYLE AND BENZOIC ACID.

Benzoate of Oxide of Ethyle. Syn. Benzoic Ether.—Discovered by Scheele. Formula, $AeO, BzO.$ Four parts of alcohol, sp. gr. 0·83, 2 parts of crystallized benzoic acid, and 1 part of concentrated hydrochloric acid, are distilled together. As soon as the product, when mixed with water, becomes milky, the receiver is changed, and the subsequent product is collected. By adding water, the ether is separated; by boiling with water and oxide of lead, it is purified from benzoic acid; and, by standing over chloride of calcium, it is freed from water and alcohol. This ether is also formed when equal volumes of chloride of benzoyl and alcohol are mixed. The mixture, slightly heated, becomes hot; hydrochloric acid passes off, and by the addition of water the benzoic ether is separated. Here the chloride of benzoyl acts on the water of the alcohol, producing benzoic and hydrochloric acids; the former of which, in the nascent state, unites with the ether of the alcohol.

Benzoic ether is a colourless oily liquid, having a feeble aromatic smell, like that of fruits, and a pungent aromatic taste. It has a sp. gr. of 1·0539 at 50°, boils at 410°, is miscible with alcohol and ether, insoluble in water; is decomposed by chlorine, (Malaguti,) producing, among other products, chloride of benzoyl.

COMPOUNDS OF OXIDE OF ETHYLE OF UNCERTAIN CONSTITUTION.

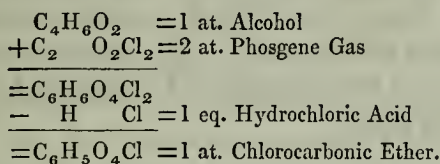
Chlorocarbonic Ether.—Formula, $C_6H_5O_4Cl.$ When phosgene gas (chlorocarbonic oxide or acid) is mixed with alcohol, a peculiar ethereal liquid is formed, to which Dumas has given the above name. Whether it contains ethyle, or its oxide, is so far uncertain, that hitherto no compound of ethyle, such as alcohol, has been obtained by its decomposition.

Prep.—Absolute alcohol is saturated with phosgene gas, when it becomes hot, and separates into two strata, the lower of which is the

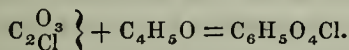
new compound. The upper contains water, alcohol, and hydrochloric acid. The new ether is purified by standing over oxide of lead and chloride of calcium, and by rectification. (Dumas.)

Prop.—A colourless, very fluid liquid, of a suffocating ethereal odour, causing a flow of tears; neutral to test paper, of sp. gr. 1.133 at 60°, boiling at about 200°; inflammable, burning with a green flame. By warm water it is resolved into hydrochloric acid and other products not yet examined. Concentrated sulphuric acid decomposes it in the cold, producing hydrochloric acid, when heated, with deposition of carbon. Ammonia resolves it into sal-ammoniac and urethane.

If to the elements of 1 at. alcohol we add those of 2 at. phosgene gas, and subtract from the whole those of 1 eq. hydrochloric acid, chlorocarbonic ether is left.



Dumas considers it as a compound of a peculiar acid with ether, which acid may be regarded as carbonic acid in which part of the oxygen has been replaced by its equivalent of chlorine.



Berzelius considers it a compound of carbonic ether with phosgene gas. $\text{C}_5\text{H}_5\text{O}_3 + \text{COCl}.$

Urethane.—Formula, $\text{C}_6\text{H}_7\text{O}_4\text{N}.$ Discovered by Dumas.

Prep.—Chlorocarbonic ether is dissolved in aqua ammoniac, when an instantaneous reaction ensues with developement of heat. The solution is evaporated to dryness in vacuo over sulphuric acid, and the dry residue distilled in a gentle heat. Urethane passes over as a colourless liquid, which consolidates on cooling, while sal-ammoniac is left behind.

Prop.—Colourless, pearly, crystalline mass, like spermaceti; fusible at 212°, volatile without change at 365°; soluble in water and alcohol, from which, by spontaneous evaporation, it separates in large crystals. Its aqueous solution has no action on metallic salts. If heated in the moist state, it is decomposed with disengagement of ammonia. Is decomposed by alkalies, the products not yet examined. In urethane the chlorine of chlorocarbonic ether is replaced by amide: $\text{C}_6\text{H}_5\text{O}_4 + \text{NH}_2.$ When the ether is acted on by ammonia, the chlorine with 1 eq. of hydrogen from ammonia forms hydrochloric acid, which combines with the ammonia in excess to form sal-ammoniac. The amide, derived from the ammonia that has lost 1 eq. hy-

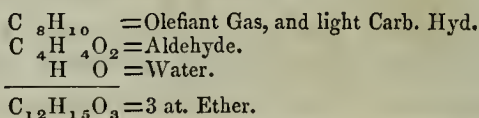
drogen, takes the place of the chlorine. It may be considered as a compound of 2 at. carbonic ether, and 1 at. urea, $2(\text{C}_5\text{H}_5\text{O}_3) + \text{C}_2\text{N}_2\text{H}_4\text{O}_2 = 2(\text{C}_6\text{H}_7\text{O}_4\text{N})$. Hence the name compounded of urea and ether. It has also the composition of anhydrous lactate of ammonia, or rather of lactamide, a body of totally different properties. Liebig has also recently discovered a third compound, derived from creatine, (a crystalline compound existing in animal flesh,) which has exactly the same composition. This new compound is a body of distinctly basic or alkaline character.

Berzelius is inclined to consider urcthrane as compound of oxide of ethyle with a coupled acid, analogous to oxamic acid, which may be called carbamic acid, and which is carbonic acid, CO_2 , coupled with carbamide, CONH_2 , just as oxamic acid is oxalic acid, coupled with oxamide. On this view, which is rendered probable by the recent discovery of other acids, which, in like manner, are coupled with their amides, urethane is the carbamate of oxide of ethyle; $\text{C}_4\text{H}_5\text{O} + (\text{CO}_2, \text{CONH}_2) = \text{C}_6\text{NH}_7\text{O}_4$.

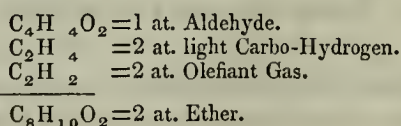
TRANSFORMATIONS AND PRODUCTS OF THE DECOMPOSITION OF ETHYLE AND ITS COMPOUNDS.

If the vapours of ether or alcohol be passed through a red-hot tube, they are resolved into inflammable gases, aldehyde, and water. The gases are mixtures of olefiant gas and light carburetted hydrogen, in which the carbon is to the hydrogen, in atoms, as 4 to 5; exactly the proportion existing in ethyle.

The empirical formula of aldehyde is $\text{C}_4\text{H}_4\text{O}_2$, and from its production it follows that 2 at. ether have given up their oxygen to a third atom. The two first atoms are resolved into olefiant gas and light carburetted hydrogen; the third, + 2 at. oxygen from the other two, yields aldehyde and water.



According to this explanation, the two carbo-hydrogens should be to each other, in volumes, as 3 to 2. Further, 2 at. ether can be resolved into 1 at. aldehyde, 2 at. olefiant gas, and 2 at. light carburetted hydrogen.



In this case, the volume of the light carbo-hydrogen would be to that of the olefant gas as 2 to 1 ; and the combustion of the mixture should yield for 4 at. carbonic acid 6 at. water.

All the decompositions which ether in other proportions undergoes at high temperatures are similar to the above ; only that the products vary. On the one hand are formed bodies containing all the oxygen ; on the other, carbo-hydrogens.

According to Masson and Dumas, when fused chloride of zinc is dissolved in alcohol, there is formed a hydrated compound of chloride of zinc with ether, which at 284° is resolved into ether which is disengaged, and water which evaporates in the gaseous ether. The ether and water are found in the receiver uncombined. If there is a great excess of chloride of zinc, the ether, at temperatures from 320° to 360° , is resolved into water and two carbo-hydrogens of unequal volatility ; one boiling at 570° , the other at 212° . The composition of the latter is C_8H_7 ; and that of the former, the less volatile, is C_8H_9 . Both together, $= C_{16}H_{16}$, have exactly the composition of olefant gas. Consequently, in their formation, 4 at. ether have been resolved into 4 at. water and these two carbo-hydrogens.

When ether is prepared from alcohol and sulphuric acid, and the raw ether in large quantity is rectified with milk of lime, there is left in the retort, swimming on the surface of the liquid, an oil, long known as the oil of wine. It is highly probable that it is a mixture of the two carbo-hydrogens just described. It is a yellow, viscid oil, of an aromatic odour, sp. gr. 0.9174 at 50° , soluble in ether, sparingly soluble in alcohol and water. It is altered by exposure to the air, becoming thick like turpentine. It is rendered white and resinous by chlorine, with formation of hydrochloric acid. Aqua potassæ renders it brown, oil of vitriol turns it black, but on the addition of water a colourless oil separates. The raw oil yielded to Dumas carbon and hydrogen in the proportion of $C_{16}H_{15}$; which result has been confirmed by Liebig.

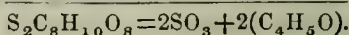
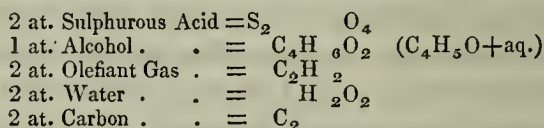
Sulphate of Oxide of Ethyle and Etherole. Syn. Sulphovinate of Etherole ; Heavy Oil of Wine.—The nature and constitution of this long-known substance were first clearly ascertained by Serullas.

Formula, $2SO_3 + C_8H_9O$.

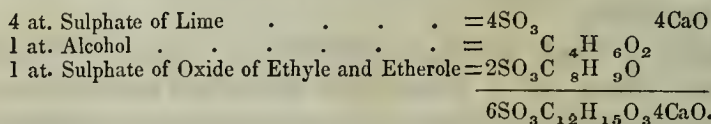
This oil is formed by the decomposition of the neutral sulphate of oxide of ethyle, a compound which cannot exist in the separate state. It is always formed when ether and anhydrous sulphuric acid directly or indirectly come in contact. If anhydrous ether be saturated with anhydrous sulphuric acid, the former is instantly resolved into alcohol, which separates, and a compound of oxide of ethyle and etherole.

Both products combine with sulphuric acid, and there are formed bisulphate of oxide of ethyle with 1 at. water, and sulphate of oxide of ethyle and etherole. Four at. sulphuric acid 4SO_3 , and 3 at. oxide of ethyle $\text{C}_{12}\text{H}_{15}\text{O}_3$, yield 1 at. bisulphate of oxide of ethyle 2SO_3 , $\text{C}_4\text{H}_5\text{O}$, HO , and 1 at. of the new oil 2SO_3 , $\text{C}_8\text{H}_9\text{O}$. Thus, from 2 at. ether is separated 1 at. water, which combines with 2 at. sulphuric acid and 1 at. ether. Along with the above products there are formed, by a different reaction, ethionic and isethionic acids. If the liquid be mixed with water, the excess of ether is separated; the sulphate of oxide of ethyle and etherole is dissolved in it, and may be obtained by evaporating the ether, while the bisulphate and the two acids combine with the water.

When sulphovinate of lime or potash is subjected to dry distillation, there are obtained the oil under consideration, alcohol, sulphurous acid; and olefiant gases, and a residue composed of carbon and a sulphate. These products are formed by two independent and simultaneous reactions. From 2 at. double sulphate of oxide of ethyle and lime are obtained 1 at. of the oil, 1 at. water, and 2 at. sulphate of lime. In the other reaction, the same materials yield the following products, along with 2 at. sulphate of lime.



By the addition of a dry fixed base, such as lime or baryta, one of these reactions is prevented. In this case, there are formed sulphate of oxide of ethyle and etherole, and hydrate of lime, which, with an atom of sulphate of oxide of ethyle, produces sulphate of lime and alcohol. Three at. double sulphate of oxide of ethyle and lime, $6\text{SO}_3 + \text{C}_{12}\text{H}_{15}\text{O}_3 + 3\text{CaO}$, with 1 at. lime, CaO , give



To obtain this substance, an intimate mixture of dry sulphovinate of lime or potash with its own weight of quicklime is distilled at a temperature not higher than about 540° . The product is freed from alcohol by evaporation in the air or in vacuo over sulphuric acid. This oil may likewise be obtained by distilling the basic sulphovinate of lead.

It is a colourless, oily liquid; heavier than water, sp. gr. 1.133;

of an aromatic ethereal odour, and a cooling taste; without action on dry vegetable colours. It boils at 540° , distilling unchanged when dry; potassium at the ordinary temperature is not tarnished in it, but decomposes it at a higher temperature. It is miscible with alcohol and ether.

In contact with water or alkalies, it is decomposed, producing hydrous bisulphate of oxide of ethyle, and etherole. Heated with sulphuret of potassium, it gives mercaptan, and a heavy oil containing sulphur. (Zeise.)

ETHEROLE AND ETHERINE.

Etherole. Syn. Light Oil of Wine.—A product of the decomposition of the substance last described. Discovered by Hennell; but most accurately studied by Serullas, according to whom it contains carbon and hydrogen in the same proportions as olefiant gas. This has lately been confirmed by Marchand.

Prep.—The heavy oil of wine is gently heated with water, and the light oil which separates is washed with water till all acid is removed. It is dried by chloride of calcium.

Prop.—A colourless oily liquid, of sp. gr. 0.917 to 0.920; boils at 536° , becomes viscid at -13° , and solid at -31° ; sparingly soluble in rectified spirits, very soluble in absolute alcohol and ether; miscible in all proportions with oil of vitriol, and separated unchanged by water: combines with anhydrous sulphuric acid, becoming brown; water separates nothing, and the acid liquid, neutralized by baryta, gives a salt which Marchand considers to be ethionate of baryta.

When etherole is left for a long time at a low temperature, it deposits crystals of etherine. Etherine, or camphor of oil of wine, has the same composition as etherole or olefiant gas, in 100 parts. When the etherole refuses to deposit more crystals in the cold, those deposited are pressed between folds of bibulous paper, and purified by solution in ether and crystallization.

Prop.—Brilliant, long, translucent, tasteless, friable prisms and plates; fusible at 230° , boiling at 500° ; sp. gr. 0.980; soluble in alcohol and ether, insoluble in water.

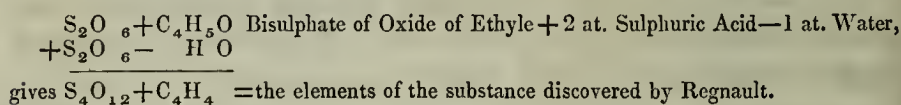
ETHIONIC AND ISETHIONIC ACIDS.

These two acids, one of which is remarkable on account of its extreme stability, were first obtained by Magnus, by bringing in contact, in the cold, alcohol and anhydrous sulphuric acid. The resulting

liquid is diluted with water, and neutralized by carbonate of baryta. There is formed, along with sulphate of baryta, which is separated by the filter, ethionate of baryta, which remains dissolved. If the solution be evaporated by a gentle heat to the consistence of syrup, and mixed with alcohol, it deposits ethionate of baryta in the form of a white powder. By the cautious addition of diluted sulphuric acid to the aqueous solution of this salt, a solution of ethionic acid may be obtained. This acid has little permanence. If its solution be boiled, the liquid contains free sulphuric acid and isethionic acid. This latter acid is also obtained by saturating pure ether with anhydrous sulphuric acid. When water is added to the mixture, the excess of ether separates, along with heavy oil of wine ($2\text{SO}_3, \text{C}_8\text{H}_9\text{O}$). The liquid below the stratum of ether is acid, and when heated gently, yields ether; when boiled, alcohol, which is thus reproduced from ether directly. The residual liquid after the boiling contains free sulphuric acid and isethionic acid.

The formation of both these acids has lately been explained by Magnus. Alcohol is decomposed by anhydrous sulphuric acid, and the compound formed is sulphate of etherole, $4\text{SO}_3 + \text{C}_4\text{H}_4$. Regnault has found that this compound can be directly produced by saturating anhydrous sulphuric acid with olefiant gas. White fusible crystals are formed, which, when dissolved in cold water, combine with one atom of water, and form ethionic acid, $4\text{SO}_3, \text{C}_4\text{H}_5\text{O}$. By boiling this solution, the ethionic acid loses 2 atoms of sulphuric acid, and is converted into isethionic acid, $2\text{SO}_3, \text{C}_4\text{H}_5\text{O}$. This discovery enables us to explain the action of dry sulphuric acid on alcohol and ether without ambiguity.

The first effect of the anhydrous acid on alcohol is to form hydrated bisulphate of oxide of ethyle. An excess of the acid decomposes the combined oxide of ethyle, depriving it of the elements of water, by which means etherole, or a substance of the same composition, is set free; which, with 4 at. sulphuric acid, produces ethionic acid and water.



Pure ether with anhydrous sulphuric acid gives water and heavy oil of wine ($2\text{SO}_3, \text{C}_8\text{H}_9\text{O}$). The water combines with the sulphuric acid to form hydrated acid, which, with another portion of ether, forms bisulphate of oxide of ethyle ($2\text{SO}_3, \text{HO}, \text{C}_4\text{H}_5\text{O}$). By the action of anhydrous sulphuric acid on the etherole there is produced, just as

with olefiant gas, which is isomeric with etherole, the substance which, in contact with water, forms ethionic acid; and, by the further action of the anhydrous acid on the bisulphate of oxide of ethyle, the same reaction occurs as with alcohol.

Under all circumstances, therefore, a mixture of alcohol or ether with anhydrous sulphuric acid contains bisulphate of oxide of ethyle, and a new substance (produced by the action of sulphuric acid on a carbo-hydrogen), which, with water, forms ethionic acid. If the liquid is boiled, the bisulphate is resolved into alcohol and sulphuric acid; the ethionic acid into sulphuric acid and isethionic acid. If it be neutralized with baryta before being boiled, we obtain ethionate of baryta and the double sulphate of oxide of ethyle and baryta. When this solution is evaporated at temperatures lower than 212° , till crystals begin to appear, on adding absolute alcohol, crystals of ethionate of baryta are precipitated, which, by being redissolved in water and again precipitated by alcohol, are rendered perfectly pure. Ethionate of baryta consists of $4\text{SO}_3, \text{C}_4\text{H}_5\text{O}, \text{BaO}$, and from it all the other salts of ethionic acid can be easily made.

Isethionic acid is obtained by cautiously adding dilute sulphuric acid to isethionate of baryta, till all the baryta is precipitated. The filtered liquid is evaporated, at first with the aid of heat, afterwards in vacuo over sulphuric acid. It is a viscid oily liquid of a very sour taste, very soluble in alcohol and ether. It bears a temperature of 302° without decomposition. At a higher temperature it is blackened. When a salt of isethionic acid is fused with a hydrated alkali, it yields free hydrogen, with carbonate and oxalate of the base, the carbon being derived from the organic part of the acid; a mixture of equal equivalents of suphate and sulphite of potash is also formed. This last character is peculiar to the hyposulphates. It is, therefore, probable, that the true formula of the isethionic acid must be $\text{S}_2\text{O}_5, \text{C}_4\text{H}_5\text{O}_2 + \text{aq.}$

The salts of isethionic acid are without exception soluble in water. The acid decomposes the salts of all organic acids, uniting with the base. It also decomposes the chlorides of the alkalifiable metals with the aid of heat, disengaging hydrochloric acid. Its salts are all neutral, and bear a heat of 480° without decomposition. The *Isethionate of ammonia* crystallizes in octohedrons. *Isethionate of potash* forms anhydrous, colourless, transparent broad plates. *Isethionate of copper*, sea-green regular octohedrons, containing 2 at. water of crystallization, which are expelled by a heat of 230° , when the crystals become milk-white. *Isethionate of silver* is very soluble, and crystallizes in brilliant broad plates. *Isethionate of lead* crystallizes in hard anhydrous needles, formed in radiated groups.

Isethionate of Baryta.—Formula, $S_2O_5, C_4H_5O_2, BaO$.

Prep.—Anhydrous sulphuric acid is placed in a U-shaped tube, and olefiant gas is made to pass through it. At first it is kept cold, afterwards it is warmed, but only to the melting point of the acid. The olefiant gas must be first passed through milk of lime to remove sulphurous acid, and afterwards through oil of vitriol to retain water. As soon as no more gas is absorbed, the mass is dissolved in water, boiled for half an hour in the diluted state, saturated with carbonate of baryta, filtered, and evaporated till it crystallizes. Or anhydrous ether, carefully cooled, is saturated with anhydrous sulphuric acid, the mixture diluted with water, when ether and heavy oil of wine separate; the acid solution is boiled as long as alcohol is given off, neutralized with carbonate of baryta, and evaporated. The salt crystallizes easily out of a very strong solution in opaque six-sided plates, which are anhydrous, permanent in the air, fusible at 392° , decomposed with frothing at a higher temperature.

When, in saturating ether with anhydrous sulphuric acid, it is not kept sufficiently cool, sulphurous acid is disengaged, the mixture blackens and is found to contain an acid different from isethionic acid, distinguished by forming with baryta a salt totally insoluble in alcohol, which crystallizes along with the isethionate of baryta, but is easily removed by alcohol. This acid has been named

Methionic Acid.—Formula of the anhydrous acid, as it exists in the salt of baryta, $S_2C_2H_3O_7$. It may be obtained from the methionate of baryta, in the same way as isethionic acid from isethionate of baryta. It is a very sour liquid, which may be boiled and evaporated without decomposition.

Methionate of Baryta.—When ether is saturated with anhydrous sulphuric acid at the ordinary temperature, and the mixture treated as above, the solution contains isethionate and methionate of baryta. When nearly about to crystallize, it is mixed with its own bulk of alcohol, which precipitates the methionate. It may be purified by solution in water and crystallization. It forms colourless, transparent, brilliant, anhydrous scales, like chlorate of potash; soluble in 40 parts of cold water, more soluble in hot water. The solution precipitates no metallic salts; the salt is insoluble in alcohol, loses no weight at 212° ; and when heated assumes a fugitive yellow colour, yields water, sulphurous acid, and sulphur. The residue contains sulphate of baryta. It is decomposed by fusion with caustic potash, but the residue contains no sulphite of potash.

Althionic Acid.—When the residue of the preparation of olefiant gas from alcohol and sulphuric acid is diluted with water, and neutral-

ized with milk of lime, a salt of lime remains in solution, which may be evaporated and crystallized without alteration. If the lime be removed from the solution of this salt by oxalic acid, a sour liquid is obtained, which when boiled yields alcohol, and then is found to contain free sulphuric acid. Regnault has named this acid Althionic acid. This reaction when heated is identical with that of sulphovinic acid (bisulphate of oxide of ethyle); and the salts, which the acid forms with bases, are exactly of the same composition as the sulphovinates. They were considered to be the same, till Ettling pointed out marked differences in the crystalline form of the salts of the two acids with the same bases; an observation confirmed by Regnault. The salts of potash, lime, and baryta crystallize with much greater difficulty than the corresponding sulphovinates. The most marked distinction is perceived in the salt of copper. The sulphovinate of that base (double sulphate of oxides of ethyle and copper) crystallizes in large azure-blue rectangular prisms or eight-sided tables; the althionate of copper in long thin rhombic plates, the acute angle of which $= 60^\circ$, of a pale colour.

The althionate of baryta, when boiled for a long time, deposits sulphate of baryta, and the liquid becomes very acid. If now saturated with carbonate of baryta, more sulphate is formed, and there remains in solution a small quantity of a soluble salt of baryta not further examined.

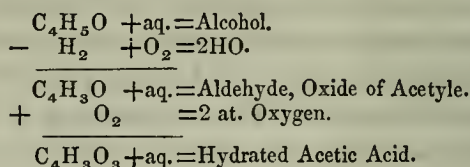
It is hardly to be doubted, that the difference in the properties of the so-called althionates and the double sulphates of ethyle and bases depend on a similar cause to that which produces the difference between the ethionates and those same salts; that is, the althionates must be double salts of isethionic acid, or an acid of the same composition, and the acid of the sulphovinates.

Products of the Oxidation of Ethyle and its Compounds, in which the number of Atoms of Carbon remains the same as in Ether and Alcohol.

1. ACETYLE AND ITS COMPOUNDS WITH OXYGEN.

It has already been mentioned, that, when nitric acid acts on ether or alcohol, different products are obtained, besides the oxides and acids of nitrogen, according to the proportion of oxygen which enters into combination with the elements of the ethyle. These are, aldehyde, acetic acid, formic acid, oxalic acid, carbonic acid, and water. The elements of ethyle possess different degrees of attraction for oxygen, the hydrogen combining more easily with it than the carbon, whence it

happens, that in the earlier stages of its action it is the hydrogen which is principally oxidized, and removed or replaced by oxygen. By the use of different oxidizing agents, these products vary in their number, that is, in the number of those simultaneously formed; but they do not vary in their mode of formation. By the slow oxidation of alcohol, by means of the oxygen of the atmosphere, in the process for forming acetic acid now often employed, water, aldehyde, and acetic acid are the only products. In this case 2 at. oxygen combine with 2 at. hydrogen of the ether, producing aldehyde, which takes up directly two more atoms of oxygen, forming acetic acid.



By the use of more powerful oxidizing agents, as a mixture of hyperoxide of manganese or bichromate of potash with dilute sulphuric acid, or the contact of red-hot platinum with the vapour of alcohol and ether, oxygen being also present, there are formed products of the oxidation of aldehyde, namely, aldehydic acid and acetic acid; and, further, products of the oxidation of these, as formic and carbonic acids. By the action of nitric acid oxalic acid is formed, which remains in the residue of the distillation. Acetic and formic acids combine easily with oxide of ethyle: hence acetate and formiate of oxide of ethyle always accompany these products; and, when nitric acid is the oxidizing agent, hyponitrite of oxide of ethyle is also formed.

When the vapour of alcohol, mixed with oxygen or air, is put in contact with spongy platinum or platinum powder, another substance is formed, namely, acetal, which must be considered as a compound of aldehyde and oxide of ethyle.

ACETYLE.

By the subtraction of hydrogen from ethyle there is produced a new radical, which is named acetylene. Aldehyde may be considered as the hydrate of the first stage of oxidation of this radical. This oxide is not, like oxide of ethyle, a base, but has rather a well-marked character as an acid-forming oxide, having itself feeble acid properties, and forming a crystalline compound with ammonia. It absorbs oxygen greedily from the atmosphere, and is converted into hydrated acetic acid. By treating its solution in water with oxide of silver, another

acid, containing less oxygen than acetic acid, is produced, which is named aldehydic acid. The compounds of acetylene with oxygen are—

Acetylene		C_2H_2	} unknown.
Oxide of Acetylene		C_2H_2O	
Hydrate of Oxide of Acetylene		$C_2H_2O + aq.$	Aldehyde.
Acetylous Acid		$C_2H_3O_2 + aq.$	Aldehydic Acid.
Acetylic Acid		$C_2H_3O_3 + aq.$	Acetic Acid.

HYDRATE OF OXIDE OF ACETYLE. ALDEHYDE.

Doebereiner observed, that, by distilling sulphuric acid, alcohol, and oxide of manganese, a liquid was obtained, which, if mixed with potash, and warmed, became brown; and that from the brown solution acids precipitated a reddish-brown resinous substance. The substance which gave rise to these phenomena was first obtained by Liebig. It is aldehyde.

Prep.—Two parts of aldehydammonia are dissolved in 2 parts of water, and mixed with a cold diluted acid, made with 3 parts of oil of vitriol and 4 parts of water. The mixture is distilled in a retort, connected with a condenser surrounded by ice, with the heat of the water-bath. The product is twice rectified with its own bulk of chloride of calcium, at a temperature from 77° to 86° , and is then pure.

Prop.—A colourless clear liquid, refracting light feebly, of a peculiar ethereal and suffocating smell. It boils at 72° . Sp. gr. at 65° , 0.79. It is miscible with water, alcohol, and ether, neutral to test paper, inflammable, burning with a pale flame. It absorbs oxygen, and is converted into hydrated acetic acid; dissolves phosphorus, sulphur, and iodine; is decomposed by chlorine and bromine. Solution of chlorine converts it into acetic acid. The same change takes place when it is heated with dilute sulphuric acid. When mixed with oil of vitriol, it becomes thick and brown, and after some time a black carbonaceous coagulum separates. When mixed with aqua potassæ, the mixture soon becomes brown, and after some time a light brown resin rises to the surface. When a solution of aldehyde is warmed with oxide of silver, the oxide is partially reduced, without disengagement of gas, and the vessel is thus covered with a brilliant surface of silver. The liquid contains aldehyde of silver. A liquid containing aldehyde, to which some ammonia is first added, and then nitrate of silver, till all alkaline reaction disappears, produces the same appearance of reduced metal when heated; and this, with the action of potash, is a sure and simple method of proving the presence of aldehyde in any liquid. When long kept, aldehyde spontaneously changes into two sub-

stances of the same composition : one of which, metaldehyde, is solid at ordinary temperatures ; the other, elaldehyde, is a liquid.

Formula of aldehyde, $C_4H_3O + aq.$

Liebig and Wöhler have lately shewn, that, when the vapour of hydrated cyanic acid is introduced into aldehyde, there is formed a new acid, which is named *Trigenic acid*. It contains the elements of

2 eqs. Anhydrous Cyanic Acid	$C_4N_2O_5$
1 eq. Aldehyde	C_4H_3O
1 eq. Ammonia	NH_3
1 eq. Trigenic Acid (Anhydrous)	$C_8N_3H_6O_3$

It is formed from 1 eq. aldehyde, and 3 eq. hydrated cyanic acid ; and during the reaction 1 eq. of anhydrous cyanic acid, with the basic water of all 3 eq., is resolved into carbonic acid which escapes, and ammonia which enters into combination. $C_2NO + 3HO = 2CO_2 + NH_3$.

This very remarkable acid, when heated, is decomposed, being charred, and giving off at the same time vapours condensing into an oily liquid, which is quinoline, a base found in coal tar, and formed also by the action of fused potash aided by heat on quinine, cinchonine, and strychnine. As quinoline has the formula $C_{18}NH_7$, or $C_{18}NH_8$, its production in this way is very remarkable, since the destructive distillation usually gives rise to compounds of lower atomic weight and less complex constitution. Possibly the true formula of trigenic acid may be $C_{24}N_9H_{18}O_9$, in which case the formation of quinoline by the action of heat would be more easily understood.

Aldehydammonia.—Doebereiner observed that raw acetal, saturated with ammonia, deposited crystals ; in which Liebig proved the presence of aldehyde.

Formula, C_4H_3O, NH_3, HO .

Prep.—Six parts of sulphuric acid, mixed with 4 of water, 4 of alcohol at 80 p. c., and 6 of hyperoxide of manganese in fine powder, are distilled by a gentle heat. The retort must be capacious, and connected, air-tight, with a receiver surrounded by ice. When no more frothing is observed in the retort, the product, which amounts to 6 parts, is rectified with its own weight of chloride of calcium. The product now amounts to 3 parts, and is again rectified with its own weight of chloride of calcium. In this way $1\frac{1}{2}$ parts are obtained of a liquid, consisting chiefly of aldehyde, with a little water, alcohol, and acetic and formic ethers. These $1\frac{1}{2}$ parts are mixed with their bulk of ether, and the mixture is saturated with dry ammoniacal gas, when crystals of aldehydammonia separate in abundance ; which, when washed with ether and dried at the ordinary temperature, are quite pure.

Prop.—Colourless, transparent, brilliant, acute rhombic prisms, re-

fracting light powerfully, friable, having an odour of turpentine, fusible between 158° and 176° , distilling unchanged at 212° . The crystals become brown by exposure to the air, and even in sealed tubes, and acquire a smell of burnt feathers. They are very soluble in water, and the solution has an alkaline reaction. They are soluble in alcohol, acetal, and acetic ether; insoluble in ether. A concentrated solution gives, with nitrate of silver, a precipitate soluble in water, insoluble in alcohol, which contains nitric acid, oxide of silver, ammonia, and aldehyde. Liebig and Wöhler have recently shewn, that, by the action of sulphuretted hydrogen on the aqueous solution of aldehydammonia, a new base is formed, to which they give the name of *thialdine*. A similar base is also obtained by means of seleniuretted hydrogen. They will be mentioned under the head of Organic Bases.

ACETAL.

Discovered by Doebereiner, and by him named oxygen ether.

Prep.—In a tall wide-mouthed bottle, containing alcohol to the depth of an inch, are suspended 3 or 4 watch-glasses, containing powder of platinum to the depth of 2 lines, near the surface of the liquid. The platinum should be moistened with water, and the bottle left for some months in a warm place. The liquid is then found to be very acid, and to contain acetal, aldehyde, acetic acid, and acetic ether. It is neutralized with chalk, and distilled. The product is treated with repeated portions of chloride of calcium till it is no longer moistened. The liquid is then rectified; and as soon as the boiling point rises to 202° , the product is pure acetal.

Prop.—A colourless, mobile liquid, of a peculiar smell, like that of Hungary wines; boiling at 204° ; sp. gr. at 68° , 0.823. Soluble in 6 parts of water, miscible in all proportions with alcohol. Is not rendered brown by potash at first; but the mixture absorbs oxygen, and then becomes brown, resin of aldehyde being formed. It is rendered thick and black by oil of vitriol. Its empirical formula is $C_8H_9O_3$; according to which, it may be considered a compound of 3 at. oxide of ethyle and 1 at. acetic acid, $= C_{16}H_{18}O_6$. But the action of potash and sulphuric acid seems to prove incontestably the presence of aldehyde; and its probable rational formula is therefore C_4H_3O, HO, AeO . a compound of aldehyde and oxide of ethyle.

PRODUCTS OF THE DECOMPOSITION AND TRANSFORMATION
OF ALDEHYDE.

Aldehyde with Potassium.—When potassium is introduced into aldehyde, heat is developed, hydrogen gas is disengaged, and a solid compound is formed, containing potash, which is soluble in water, has an alkaline reaction, reduces the salts of silver with the aid of heat, and is decomposed by acids, without yielding aldehyde. This compound has not been minutely examined; it is probably aldehydate of potash, or contains that substance.

Resin of Aldehyde.—A product of the decomposition of the aqueous solution of aldehyde by caustic potash. It is likewise produced when an alcoholic solution of potash is exposed to the atmosphere. The reaction has not been fully studied, yet it is known that the resin of aldehyde is not the only product. A mixture of potash with aldehyde and water, when heated, gives off a combustible liquid, of a most penetrating odour, which smarts the eyes very powerfully, the composition of which is unknown. The resin swims on the surface of the liquid in the retort, in the shape of a soft light-brown mass, very soluble in alcohol and aqua potassæ, from which it may be obtained by evaporation, or by saturating with an acid. When dried and heated to 212° , it gives off a very nauseous soapy smell, and it sometimes happens that it inflames spontaneously.

Elaldehyde.—Isomeric, or rather polymeric with aldehyde. When pure aldehyde is long kept, it loses by degrees its solubility in water, and produces two new substances. If kept at 32° , it forms ice-like needles, which melt at about 35° into a transparent liquid, lighter than water. It has the odour of aldehyde, but weaker; it boils at 201.5° . It does not become brown with potash, nor does it act on nitrate of silver. It does not combine with ammonia. Its composition in 100 parts is exactly that of aldehyde, but the density of its vapour shows that 3 vol. of vapour of aldehyde have been condensed into one volume of elaldehyde.

Empirical formula, $C_{12}H_{12}O_6$. (Fehling.)

Metaldehyde.—When aldehyde is kept at the ordinary temperature, it is partially converted into crystals of metaldehyde, which sometimes disappear without apparent cause. It forms long, hard, four-sided prisms, friable, volatile at 230° without previously melting. The vapour condenses in the air in the form of a light snow. It is insoluble in water, soluble in alcohol, out of which it may be crystallized. It has also the same composition in 100 parts as aldehyde; but doubtless

the density of its vapour is different, although that is not yet ascertained. (Fehling.)

From the great tendency of aldehyde to be converted into bodies possessing different properties, probably arises the circumstance, that, by the action of chlorine on it, many new compounds are formed, which are quite different from those produced in alcohol by the same agent. Some experiments, made with the view of forming chloral from aldehyde, succeeded so far as to produce a liquid having most of the properties of chloral; but in many other experiments substances totally different were obtained. But the fact that chloral (as will be shewn hereafter), as well as aldehyde, is prone to undergo spontaneous conversion into a compound isomeric or polymeric with itself, without the aid of any reagent, is strong proof of an analogy in the constitution or internal molecular arrangement of these two substances.

Aldehydic Acid. Syn. Acetylous Acid; Lampic Acid.—The name of aldehydic acid has been given to the acid which is formed when an aqueous solution of aldehyde is warmed with oxide of silver. In this case, as above mentioned, part of the oxide of silver is reduced, and the rest combines with the new acid. If a current of sulphuretted hydrogen be passed through the liquid, the silver is separated as sulphuret, and the aldehydic acid is obtained pure, but much diluted. It is sour, and neutralizes metallic oxides; but its salts cannot be obtained pure, because when evaporated they pass into acetates, with the deposition of a brown substance resembling the resin of aldehyde. In vacuo they are obtained of a yellow colour. Their characteristic property is to yield with cold sulphuric acid a vapour which attacks the eyes strongly, while the mixture becomes black. If a solution of aldehydate of baryta be warmed with oxide of silver or of mercury, these metals are reduced without effervescence, and the solution is found to contain pure acetate of baryta. The following considerations leave no doubt as to the composition of this acid:—

Aldehyde, gently warmed with oxide of silver, gives metallic silver and a soluble salt of oxide of silver. The latter may be safely assumed to contain 1 at. oxide of silver. If now the solution of this salt be mixed with as much barytic water as precipitates all the oxide of silver, and the solution, which now contains the acid combined with baryta, be heated along with the oxide of silver just formed, the latter is completely reduced, and the liquid now contains pure acetate of baryta. In this salt the oxygen of the acid is to that of the base as 3 : 1; but 1 of these 3 at. of oxygen was combined with oxide of silver in the aldehydate, the salt first formed, and passed from the

silver to the aldehydic acid, converting it into acetic acid. Now acetic acid in its dry salts has the formula $C_4H_3O_3$; consequently, the dry aldehydic acid must have the formula $C_4H_3O_2$, or in the state of hydrate $C_4H_3O_2 + aq$.

Aldehydic acid is in all probability one ingredient of the so-called lampic acid, discovered by Davy and Faraday, and more closely examined by Daniell and Arthur Connell. When a coil of platinum wire is kept red hot in the wick of a spirit-lamp, and the products of this imperfect combustion condensed in a proper apparatus, an acid liquid is obtained, the vapour of which acts strongly on the eyes, and which contains several acids, one of which is formic acid. (Connell.) Daniell neutralized this acid liquid, which he called lampic acid, with alkalies, and obtained salts, the composition of which approached nearly to that of acetates, but which differed from them by their action on the salts of silver and mercury; the solutions of which, heated with the new salts, deposited reduced metal, with disengagement of carbonic acid gas, while a part of the oxides was found dissolved in the form of acetates. This induced Connell to pronounce the lampic acid a mixture of acetic and formic acids: but the solutions of its alkaline salts become brown by evaporation, and the acid itself is blackened by sulphuric acid; characters which do not belong to either acetic or formic acids, but rather to aldehydic acid. Besides, acetic and formic acids, although both have a pungent smell, do not affect the eyes, which the lampic acid does, and which is remarkably the case with aldehydic acid. Hence it is probable that lampic acid is a mixture of aldehydic, acetic, and formic acids. A part of the acetic acid obtained from it is probably formed from aldehydic acid as above. A comparison of the lampic acid with the aldehydic acid prepared directly from aldehyde will soon decide the question.

ACETYLIC ACID.—ACETIC ACID.

Vinegar has been known from the earliest periods, and pure hydrated acetic acid was first obtained by Löwitz in 1793. All liquids which are capable of the vinous fermentation may be made to produce vinegar. In all such liquids sugar is present, which is first, by fermentation, converted into alcohol, and afterwards, by oxidation, into acetic acid.

The process was called the acetous fermentation, but has nothing in common with the true vinous fermentation, except that the presence of a ferment is necessary; for in the latter the operation, once begun, goes on in close vessels, while the presence of oxygen or air is throughout essential to the former. The nature of

the acetification of alcohol was first clearly developed by Doeberiner, from a consideration of the very remarkable fact, observed by E. Davy, that the vapour of alcohol, in contact with platinum powder, caused the powder to become red hot, and was itself converted into acetic acid. Doeberiner shewed that oxygen is essential in this experiment, and further proved that 1 at. alcohol, to form acetic acid, absorbed 4 at. oxygen. The composition of acetic acid being known, it followed that these elements must yield 1 at. dry acetic acid and 3 at. water.

$$\text{C}_4\text{H}_6\text{O}_2 + \text{O}_4 = \text{C}_4\text{H}_3\text{O}_3 + 3\text{HO}.$$

The way in which this change occurs has been already explained under Acetylene.

In the ordinary mode of preparing vinegar certain substances are necessary, the nature and precise action of which are still obscure, such as ferment or similar matters; but it is certain that they only act in contributing to the conversion of alcohol into acetic acid, by virtue of the power they possess of causing the alcohol to absorb oxygen from the air. This power appears to belong to all bodies in a state of *cremation*, or slow oxidation.

Pure alcohol, or spirits free from all impurity but water, does not become acid by exposure to the atmosphere; while in fermented liquids, the alcohol, being mixed with various organic matters, when placed in a proper temperature, quickly disappears, and is replaced by acetic acid. The same takes place with alcohol to which have been added certain organic substances, such as extract of malt, honey, wine, lees of wine, yeast, or even ready-made vinegar. From a careful consideration of all the phenomena, it is evident that these substances act by contact, communicating to the particles of alcohol their own state of activity. They are themselves, however, altered by degrees, and converted into substances insoluble in water. When this change is produced at a temperature at which the alcohol is not oxidized, the liquid, by the removal of these substances, loses its power of forming vinegar in a higher temperature. This often happens in wine; and Bavarian beer is a beer which has been made to ferment at a low temperature, till all the matters which favour acetification have been rendered insoluble.

Some have been disposed to ascribe the acetification of alcohol to a new force, called catalysis, whereby the mere contact of certain bodies causes combinations and decompositions. But we know that an alloy of platinum and silver dissolves in nitric acid, while platinum alone does not. Here the contact of silver in a state of oxidation causes the platinum to assume the same condition. There is no occasion, therefore, to have recourse to a new and mysterious power, as it is very plain

that the organic matters alluded to promote the acetification, as the silver does, by communicating mechanically their own state to the alcohol. The foregoing remarks will serve to explain the theory of ordinary acetification, or the making of vinegar.

On the small scale, 100 parts of water, 13 of brandy, 4 of honey, and 1 of winestone or tartar, or 120 parts of water, 12 of brandy, 3 of brown sugar, 1 of tartar, and $\frac{1}{2}$ of sour dough, if left for some weeks in a warm place, yield a strong and pleasant vinegar.

On the large scale, an infusion of malt, which has previously undergone the vinous fermentation, is mixed with a little sour dough or other ferment, and left in a warm chamber with free access of air, till the acetification is complete.

In wine countries, inferior wines, which have already become somewhat sour, are employed. The wine is mixed with a little vinegar, and exposed to the air in casks, partly filled with the pressed husks of the grapes. From time to time the liquid is drawn off below, air supplies its place, and the husks become warm by absorbing oxygen, which they yield to the alcohol when it is again poured into the vessel. By repeating this process, the acetification goes on rapidly. The addition of more or less brandy enables the manufacturer to procure vinegar of any desired strength.

By attending strictly to all the circumstances, such as temperature, free access of air, exposing a large surface of liquid, &c., which favour the oxidation of alcohol, the time necessary to produce vinegar may be greatly curtailed. This is done in the improved method of acetification. In this, the liquid to be acetified, namely, 1 part alcohol at 80 p. c., 4 to 6 parts of water, and $\frac{1}{1000}$ of ferment, honey, or extract of malt, is made to trickle down through a mass of shavings steeped in vinegar. By this means the surface exposed to the air is prodigiously increased. The liquid is first warmed to between 75° and 83° ; but the temperature quickly rises to 100° or 104° , and remains stationary at that point while the action goes on favourably. When the liquid has been three or four times passed through the cask with shavings, it is found to be completely acetified. This requires from 24 to 36 hours. All fermented liquors may be acetified in this way. Should the supply of air be deficient, the alcohol is not entirely acetified, part of it remaining in the state of aldehyde, which, being volatile, flies off and causes a corresponding loss of acetic acid. In some manufactories great loss was sustained from this cause; which Liebig, after his discovery of aldehyde, was enabled to detect, and completely to obviate. The presence of essential oils, or the smallest trace of pyroligneous acid, prevents the acetification of alcohol.

An ounce of good vinegar ought to saturate 30 to 32 grains of pure and dry carbonate of potash. Such vinegar contains about 5 p. c. anhydrous acetic acid. Its sp. gr. is 1.01 to 1.03.

The adulteration of vinegar with sulphuric or hydrochloric acid is detected by nitrate of baryta or of silver; but it must be borne in mind that most vinegars contain naturally a trace of sulphates. Vinegar also contains tartaric acid, which precipitates with baryta and silver; but the precipitates are soluble in nitric acid.

The pleasant refreshing odour of good vinegar is derived from acetic ether. There are wine vinegars, beer vinegars, and malt vinegars, which, besides acetic ether, contain respectively all the foreign matters of the wine, beer, or infusion of malt. All of them yield by distillation a purer and somewhat weaker acid, *distilled vinegar*. The vinegar made from brandy by the process above described is as pure as distilled vinegar.

Pyroligneous Acid; Wood Vinegar.—By the dry distillation of wood this vinegar is obtained, at first charged with the oil of tar, from which it is freed by rectification, and by neutralization with soda. The impure acetate of soda is purified as will be hereafter described, and decomposed by sulphuric acid, when a colourless acetic acid is obtained, much stronger than distilled vinegar. It is reduced with water, but of course has not the same flavour as those vinegars which contain acetic ether, &c. The impure pyroligneous acid contains many products of destructive distillation; among others, creosote, which communicates to it a high degree of antiseptic power. Meat preserved by it acquires from the creosote a very agreeable smoked flavour.

PURE HYDRATED ACETIC ACID.

Prep.—1. Three parts of dry, finely powdered acetate of soda (from pyroligneous acid) are mixed, in a capacious retort, with 9.7 parts of purified oil of vitriol. Sufficient heat is developed by the action to cause $\frac{1}{3}$ of the acetic acid to distil over without fire. Heat is then applied till the mass in the retort becomes entirely liquid. The product is rectified, and yields 2 parts of very pure acid, containing 20 p. c. water. The later portions that distil over, exposed in a close vessel to a temperature below 40°, deposit crystals of hydrated acetic acid: the liquid portion, which is somewhat weaker, being poured off, the crystals are melted and again crystallized by cooling. When the liquid this time is poured off, the hydrate may be considered pure.—2. Three parts of dried acetate of lead are distilled with 8 parts of oil of vitriol, and the product treated as above. If it contain sulphurous acid, this is

removed by agitating with peroxide of lead before rectifying. Acid containing 20 p. c. of water yields a good deal of its superfluous water to dry sulphate of soda. If poured off from the salt, and then rectified, it yields a large proportion of the crystallizable hydrate.

Prop.—Hydrated acetic acid crystallizes at temperatures below 62° in colourless, transparent, brilliant, broad scales and tables; fusible at 62° , forming a liquid of sp. gr. 1.063, of a very penetrating, peculiar, and agreeable odour, and a most pungent acid taste. It acts strongly on the skin, causing redness and blistering. It boils at about 248° , fumes slightly in a moist atmosphere, and attracts moisture from it. It is miscible in all proportions with water, alcohol, and ether, also with essential oils; and it dissolves camphor and various resins. Its vapour is inflammable. Sulphuric acid added to it, causes heat and blackening, with disengagement of sulphurous acid gas. Nitric acid exerts no peculiar action on it. It is not decomposed by chlorine in the dark, and when cold; but, with the aid of the sun's rays, the chlorine removes part of the hydrogen as hydrochloric acid, while the hydrogen is replaced by another portion of chlorine, forming a new acid, *chloracetic acid*. The vapour of acetic acid, passed through a tube at a low red heat, is resolved into carbonic acid and acetone; at a higher temperature it produces inflammable gases with deposition of carbon.

Formula of hydrated acetic acid, $C_4H_3O_3 + HO$.

When hydrated acetic acid is mixed with a certain proportion of water, condensation takes place, and the sp. gr. of the diluted acid is greater than that of the concentrated. When equal weights are employed, the resulting acid has the same sp. gr. as the pure hydrate. A mixture of 77.2 hydrated acid, and 22.8 water, has the highest sp. gr. = 1.079. It boils at 220° . This acid contains exactly 3 at. water to 1 at. anhydrous acid. It is obvious that the sp. gr. is no test of the strength of the acid, since with certain limits the same sp. gr. belongs to acid of two different strengths. This phenomenon does not occur in other acids, in all of which the sp. gr. diminishes in proportion to the water which is added, while in the acetic acid it increases up to the point above mentioned, and beyond that again diminishes, with the addition of water.

The hydrated acid, holding camphor and essential oils in solution, constitutes the aromatic vinegar of the shops, which is used as a stimulus against fainting, and externally as a rubefacient. Common and distilled vinegar are used in pharmacy for preparing many remedies, and externally in medicine in the form of lotions. The use of vinegar as a condiment is universal. It is likewise the antiseptic ingredient in

pickles. The raw pyroligneous acid is, however, a far more powerful antiseptic than ordinary vinegar, owing to the creosote it contains, which gives a smoked flavour to meat preserved by means of it. The purity of vinegar or acetic acid is easily ascertained. When diluted, it should give no precipitate with salts of baryta or silver; and when boiled with solution of indigo, it ought not to change the colour. Nitric acid, if present, would give to the indigo a yellow colour.

ACETIC ACID AND BASES.

Acetic acid forms, with ammonia and metallic oxides, soluble salts. The acetates of silver and protoxide of mercury are sparingly soluble. The oxygen of the base is to that of the acid, in the neutral acetates, as 1 to 3. Acetic acid forms also basic salts, with $1\frac{1}{2}$ and 3 times as much base as in the neutral acetates. The fixed alkaline acetates and those of the alkaline earths, when exposed to heat in close vessels, yield water and acetone, (see acetone,) and leave a residue of the carbonate of the base. Other acetates yield a mixture of acetic acid and acetone; while the metallic oxide, or sometimes even the reduced metal, is left. The solutions of the alkaline acetates become mouldy when kept.

All acetates, when oil of vitriol is poured over them, give off vapours of acetic acid, easily recognized by its smell. The acetates of potash and soda may be mixed with the salts of peroxide of iron, oxide of chromium, and peroxide of tin, without precipitation; but, if the mixture be heated, these oxides are entirely precipitated as basic salts, which, if left in the solution, are redissolved on cooling.

Acetate of Oxide of Ethyle. Syn. Acetic Ether.—*Prep.*—Sixteen parts of dry acetate of lead, $4\frac{1}{2}$ of alcohol, and 6 of oil of vitriol; or 10 parts of crystallized acetate of soda, 15 of oil of vitriol, and 6 of alcohol at 80 to 85 p. c., are distilled together. The product is rectified with slaked lime and chloride of calcium, to remove acid and water, and a quantity of acetic ether equal in weight to the alcohol is obtained. It may also be obtained by distilling hydrated acetic acid with sulphovinate of potash.

Prop.—A colourless liquid, inflammable, and burning with a yellow flame; of a very agreeable, refreshing odour; boiling at 165° , sp. gr. 0.89 at 60° ; neutral to test paper; soluble in 7 parts of water, in alcohol and ether in every proportion. It is very easily decomposed by alkalies. Oil of vitriol resolves it into ether and acetic acid.

Formula, $C_4H_5O + C_4H_3O_3$, or $AeO + \bar{A}$.

Acetic ether enters into the composition of various remedies in use

on the Continent. As a solvent, its properties resemble those of ether, and it might probably be employed advantageously in the preparation of varnishes, from its power of dissolving resins and essential oils.

Acetate of Ammonia.—When equal weights of sal-ammoniac and acetate of potash are distilled together, ammonia is expelled, and binacetate of ammonia distils over as an oily liquid, which on cooling forms a radiated mass of transparent needles, which is deliquescent and soluble in alcohol. By passing dry ammonia into the melted binacetate, it becomes solid, and is converted into neutral acetate, which forms a white inodorous mass, very soluble in water and alcohol, resolved by heat into ammonia and binacetate.

Formula, $\text{NH}_3, \text{HO}, \text{C}_4\text{H}_3\text{O}_3$, or $(\text{NH}_4) \text{O} + \bar{\text{A}}$.

A diluted solution of this salt is much used as a diaphoretic in febrile diseases, under the name of *Liquor acetatis ammoniæ*, formerly *Spirit of Mindererus*. It is generally made by exactly neutralizing distilled vinegar with carbonate of ammonia. As distilled vinegar, however, varies much in strength, a better formula is to neutralize 6 parts of *aqua ammoniæ*, sp. gr. 0.96, with strong acetic acid, and to add as much water as makes up 24 parts. This solution is somewhat stronger than that of the British pharmacopœias; but it is uniform, and can easily be reduced.

Acetate of Potash.—Prepared by saturating pure vinegar with carbonate of potash, and evaporating to dryness, taking care always to have a slight excess of acid present, without which the salt turns yellow or brown. It crystallizes with difficulty, and is generally obtained in a soft fibrous mass, which feels unctuous to the touch, and has a warm, pungent, sweetish, and saline taste. It deliquesces in the atmosphere, and must be kept in closely stoppered bottles. It is soluble in alcohol, and the solution is decomposed by a current of carbonic acid gas; bicarbonate of potash is deposited, and acetic ether is formed. The aqueous solution of acetate of potash absorbs chlorine, and acquires powerful bleaching properties. The dry salt, distilled with arsenious acid, yields alkarsine, or oxide of cacodyle. Acetate of potash exists in the juice of many plants, and when they are incinerated passes into carbonate of potash. Acetate of potash is a powerful diuretic, and is frequently used in medicine.

Formula, $\text{KO} + \bar{\text{A}}$.

Acetate of Soda.—Prepared on the small scale as the preceding salt. Or by precipitating acetate of lead with an excess of carbonate of soda, neutralizing the filtered liquid with acetic acid, evaporating to the consistence of syrup, and allowing it to cool slowly. (Acetate of potash may also be prepared in this way.) On the large scale, acetate of soda

is prepared from the raw pyroligneous acid, for the purpose of yielding pure acetic acid. The following is an outline of the process. The raw acid is rectified, neutralized with chalk and milk of lime; and, when the solution of acetate of lime is concentrated and hot, sulphate of soda is added. A double salt of sulphate of soda and sulphate of lime is precipitated, and the filtered liquid contains acetate of soda. It is more economical to neutralize the raw acid directly by sulphuret of sodium. Any trace of lime is removed by a little carbonate of soda; and the liquid is evaporated in leaden vessels till it has the sp. gr. 1.356, and then put to crystallize in earthenware pans. The crystals which are deposited, and which are impure, are next melted in an iron pot at a moderate heat, and roasted as long as empyreumatic oil comes off. The black carbonaceous residue is digested with cold water, and the filtered liquid is evaporated for a second crystallization. The salt thus obtained serves for the preparation of the commercial pyroligneous acid, of sufficient purity to be used as vinegar when reduced with water. If it be required to prepare perfectly pure acid, the acetate of soda must be subjected to a second fusion and a third crystallization, when it is obtained snow-white. To prepare the wood vinegar of commerce, which generally requires seven waters to reduce it to the strength of ordinary vinegar, 10 parts of acetate of soda, once fused, in crystals, are distilled with 6 parts of oil of vitriol.

Prop.—Acetate of soda, by slow evaporation, crystallizes in transparent, oblique, rhombic prisms, of a pleasant cooling saline taste. Is soluble in 3 parts water at 60°, in 5 parts alcohol; effloresces in a dry air; when heated, melts first in its water of crystallization, frothing much; in a higher temperature the dry salt again melts, and bears a low red heat without decomposition. The melted salt, on cooling, splits with a loud noise in all directions. If deliquescent, it is contaminated with acetate of potash.

Formula, $\text{NaO}, \bar{\text{A}} + 6 \text{ aq.}$

Acetate of Baryta.—Prepared by dissolving carbonate of baryta or sulphuret of barium in acetic acid, and evaporating the filtered liquid. It forms large, transparent, oblique, rhombic prisms, or irregular eight-sided prisms, very soluble, when allowed to evaporate spontaneously. These crystals contain 3 at. water, and are efflorescent. When evaporated at temperatures above 60°, the crystals contain only 1 at. water. Formula, $\text{BaO} + \bar{\text{A}} + \text{aq.}$ It is used in analysis to precipitate sulphuric acid, where it is desirable not to introduce nitric or muriatic acid.

Acetate of Strontia.—Crystallized above 60°, contains 1 at. water

to 2 at. dry salt; by spontaneous evaporation it yields crystals with 4 at. water, which are efflorescent.

Formula, $2(S_2O_3\bar{A}) + aq.$

Acetate of Lime is obtained from pyroligneous acid, as above described. Crystallizes in silky needles of an astringent, bitter, and saline taste. Effloresces at 212° ; and if heated to 226° , and triturated in the dark, it phosphoresces strongly. Is used for the preparation of acetic acid, acetate of soda, and acetates of lead and copper, &c. from pyroligneous acid.

Formula, $CaO + \bar{A} + aq.$

Acetate of Magnesia.—A very soluble, bitter salt, which crystallizes with difficulty.

Formula, $MgO + \bar{A}.$

Acetate of Alumina.—Prepared by precipitating acetate of baryta with sulphate of alumina. It is uncrystallizable, and dries into a gummy mass, very soluble in water, of a very astringent taste. Heat resolves it into acetic acid and an insoluble basic salt of alumina. The solution may be boiled without decomposition, but possesses the valuable property of depositing when heated a quantity of an insoluble basic salt, if previously mixed with a neutral salt of a mineral acid. Such a mixture, if concentrated, forms, when heated, a gelatinous paste, which disappears on cooling. These properties give to the acetate of alumina a high value in the art of dyeing, as it serves to give to the cloth, by means of the alumina it deposits on it, the power of combining with colouring matter, for which alumina has a remarkable affinity. Such a substance is called a mordant. That commonly used is made by mixing solutions of alum and acetate of lead, in such proportions that all the sulphate of potash of the alum remains undecomposed (100 alum to 120 sugar of lead). The liquor is thickened and stamped on the parts which it is wished to impregnate with the mordant. The cloth is then heated, the acetic acid flies off, and the aluminous precipitate adheres so firmly to the cloth that it cannot be washed away. If the cloth be now immersed in a coloured bath, the colour adheres only to those parts on which the mordant was stamped. If a piece of cloth be heated in a diluted solution of the mordant, and then washed, and immersed in the colour, it will be dyed all over, every part being impregnated with alumina.

Formula, $Al_2O_3 + 3\bar{A}.$

Acetate of Manganese.—Prepared by adding pure sulphate of manganese to acetate of lime. It is soluble and crystallizable, and is used in dyeing. It is printed on the cloth, and, when passed through a

bath of chloride of lime, a rich brown oxide of manganese is deposited on the cloth.

Formula, $\text{MnO} + \bar{\text{A}}$.

Acetate of Zinc.—Prepared by dissolving zinc or oxide of zinc in acetic acid. It crystallizes in flexible, brilliant, tabular crystals of a pearly talc-like lustre. By spontaneous evaporation it forms a beautiful dendritic efflorescence. It is, unlike the other salts of zinc, completely precipitated by sulphuretted hydrogen, if neutral. It is used in medicine for the same purposes as the sulphate, and in pharmacy for preparing cyanide of zinc.

Formula, $\text{ZnO} + \bar{\text{A}} + 3 \text{ aq.}$

Acetate of Protoxide of Iron.—Prepared by dissolving iron in acetic acid, or by mixing green vitriol with acetate of lead. Should any peroxide be present, it may be reduced to protoxide by sulphuretted hydrogen, a little free acid being previously added. It crystallizes in small needles, which are very soluble in water, and attract oxygen rapidly from the air. It forms, when dissolved in alcohol, the tinctura acetatis ferri, not now much employed. It is used as a mordant in dyeing.

Formula, $\text{FeO} + \bar{\text{A}}$.

Acetate of Peroxide of Iron.—Prepared by dissolving well-washed hydrated peroxide of iron in acetic acid, or by precipitating acetate of baryta with persulphate of iron. It does not crystallize; and like acetate of alumina, when heated with neutral salts, deposits an insoluble basic salt of peroxide. Hence it is much used as a mordant, having the great advantage, that the acid does not corrode or injure the cloth. It also enters into the composition of some obsolete remedies.

Formula, $\text{Fe}_2\text{O}_3 + 3\bar{\text{A}}$.

Acetate of Cobalt is red in solution, blue when dry. Mixed with common salt, it forms a good sympathetic ink. The characters are hardly visible till heated, when they become green.

Acetate of Nickel.—Green crystals, soluble in 6 parts of water. Both this and the preceding salt are completely precipitated by sulphuretted hydrogen when neutral, but not if free acetic acid be present.

Acetate of Lead. 1. *Neutral*. *Syn. Saccharum Saturni*; *Sugar of Lead*.—This well-known salt is prepared either by dissolving litharge (protoxide of lead) in acetic acid, or by the action of acetic acid on metallic lead with the aid of heat. When prepared with litharge, it contains copper, which may be completely separated by digesting the solution with a little metallic lead. It is then evaporated to crys-

tallize, with the addition of a little free acid. When it is to be made with metallic lead, the lead in thin leaves is exposed, half immersed in the acetic acid, to heat and air. In these circumstances it is very rapidly oxidized, and the oxide is dissolved by the acid. Sugar of lead crystallizes in transparent right rhombic prisms, or in needles. It has a sweetish metallic taste, and is astringent. It is poisonous, chiefly from its tendency to pass into carbonate. When gently heated, it loses water of crystallization, and becomes anhydrous; it is very apt to melt in the earlier stages of the drying, which impedes the operation. The dry salt, more strongly heated, yields much acetone, and leaves a finely divided mixture of carbon and metallic lead, which is a pyrophorus. Sugar of lead is soluble in $1\frac{1}{2}$ parts of water at 60° , and in 8 of alcohol. Aqua ammoniæ does not precipitate the aqueous solution in the cold, but produces a basic salt; if boiled with it, oxide of lead is precipitated in a crystalline form.

Formula, $\text{PbO}, \bar{\text{A}} + 3 \text{ aq.}$

Acetate of lead is much used as an astringent and styptic in diarrhœa, dysentery, and hæmorrhages. It may be safely given in large quantity if vinegar be taken along with it to prevent the formation of carbonate, which is the really poisonous compound.

2. *Sesquibasic Acetate of Lead.*—Dry neutral acetate of lead is fused by a moderate heat, until the liquid mass spontaneously forms a white porous mass, which is dissolved in water; the solution evaporated to the consistence of syrup, and set aside. It forms pearly six-sided scales in concentric groups, permanent in the air and in vacuo, very soluble in water and alcohol, alkaline to test paper.

Formula, $3\text{PbO} + 2\bar{\text{A}}.$

3. *Trisacetate of Lead.* *Syn. Subacetate of Lead.*—A cold saturated solution of neutral acetate is mixed with one-fifth of its volume of aqua ammoniæ and set aside, when the trisacetate is deposited in long needles, which are anhydrous and soluble in water. Or, to obtain it in solution, 7 parts of litharge are digested, with frequent agitation, with a solution of 6 parts of sugar of lead in 30 of water, till the oxide which remains undissolved has become quite white.

The solution, evaporated in a retort, to exclude carbonic acid, which it rapidly absorbs, forms a white opaque mass, consisting of minute needles, very soluble in water. The liquor plumbi subacetatis of the pharmacopœias is a solution of this salt, generally containing some neutral acetate. It is much used as a lotion, and has long been known as Goulard's extract, or Goulard's water. It has a strong alkaline reaction, and absorbs carbonic acid from the atmosphere, becoming tur-

bid from the deposition of carbonate. For this reason it is far more poisonous than the sugar of lead, as it has a much greater tendency to form the very poisonous carbonate. It precipitates solution of gum, and is used as a test for that substance. It yields precipitates with almost all organic acids, even those which are not precipitated by the neutral acetate. It further precipitates albumen, caseous matter, and extractive matter, and is much employed to remove such substances from organic mixtures.

Formula, $3\text{PbO} + \bar{\text{A}}$.

4. *Sexbasic Acetate of Lead*.—Prepared by adding the solution of the preceding salts to an excess of ammonia. It forms a white precipitate, composed of minute crystals, slightly soluble in hot water, from which it crystallizes on cooling. White lead is commonly a mixture of this salt with carbonate of lead.

Formula, $6\text{PbO} + \bar{\text{A}}$.

Acetate of Copper. 1. *Neutral*.—Prepared by dissolving verdigris (see below) in acetic acid with the aid of heat, and crystallizing. It appears in two forms: in dark green, oblique, rhomboidal prisms, which gradually become opaque in the air; formula, $\text{CuO}, \bar{\text{A}} + \text{aq.}$; and in oblique four-sided prisms, of a beautiful blue colour, which form when the solution crystallizes at temperatures below 46° ; formula, $\text{CuO}, \bar{\text{A}} + 5 \text{aq.}$ The latter crystals, when heated to 86° , split up into small crystals of the former variety, giving off 4 at. water. Acetate of copper, heated in the air, burns with a lively green flame. If heated in close vessels, it gives off acetic acid and acetone, and leaves finely divided metallic copper, which is easily inflammable. The solution, boiled with sugar or honey, deposits minute octohedral crystals of suboxide of copper.

Diacetate of Copper. *Syn. Verdigris; Ærugo*.—It is prepared by exposing plates of copper to the vapours of acetic acid in a warm situation. The verdigris forms on the surface of the copper, and is scraped off from time to time. It forms a bluish-green or green powder, which is resolved by cold water into soluble sesquibasic acetate and insoluble tribasic acetate or trisacetate of copper. It is chiefly used as a pigment, or in the preparation of other pigments, as Schweinfurt or Vienna green.

Formula, $2\text{CuO}, \bar{\text{A}} + 6 \text{aq.}$, or $(\text{CuO}, \bar{\text{A}}, 5 \text{aq.} + \text{CuO}, \text{aq.})$

Sesquibasic Acetate of Copper.—Is dissolved out of verdigris by water, and forms, when dry, a blue amorphous mass, easily soluble in hot water. It exists in considerable quantity in the blue varieties of verdigris. Formula, $3\text{CuO}, 2\bar{\text{A}} + 6 \text{aq.}$

Trisacetate of Copper.—A green insoluble powder, left undissolved when verdigris is acted on by water. Is the principal ingredient of verdigris, especially the green variety.

Formula, $3\text{CuO}, \bar{\text{A}}, 3 \text{aq.}$

By boiling any of the preceding basic salts for a long time with water, there is left a liver-brown powder nearly insoluble, which is an acetate with a still greater proportion of base. It contains 92 p. c. oxide of copper, according to Berzelius.

Schweinfurt or Vienna Green.—When boiling solutions of equal weights of neutral acetate of copper and arsenious acid are mixed, the mixture added to its own volume of cold water, and the whole allowed to stand for some days, a beautiful green powder is obtained, which is much prized as a pigment under the above name. When boiled with caustic potash, it leaves suboxide of copper, while arsenic acid is formed.

Acetate of Protoxide of Mercury.—Prepared by mixing hot solutions of protonitrate of mercury and acetate of potash. It is deposited on cooling in white silvery scales, which must be washed with a little cold water, and dried by pressure in bibulous paper in a dark place, as it is decomposed by light.

Formula, $\text{HgO}, \bar{\text{A}}.$

It is a pharmaceutical preparation, and occasionally used in medicine.

Acetate of Peroxide of Mercury.—Prepared by dissolving red oxide of mercury in acetic acid, and evaporating. It forms white scaly crystals, soluble in 4 parts of water, decomposed by boiling water.

Formula, $\text{HgO}_2, \bar{\text{A}}.$

It is now rarely used; but, along with the preceding salt, entered into the composition of Keyser's pills, once a celebrated remedy on the Continent.

Acetate of Silver.—Obtained by dissolving oxide of silver in acetic acid; or by mixing hot saturated solutions of nitrate of silver and acetate of potash. It is sparingly soluble, and crystallizes, on cooling, in pearly flexible needles. When heated, acetic acid is given off, and pure silver is left. It is used as a test for hydrochloric acid, particularly in testing the purity of acetates.

Formula, $\text{AgO}, \bar{\text{A}}.$

PRODUCTS OF THE DECOMPOSITION OF ETHER AND ITS
COMPOUNDS BY CHLORINE.

The changes which are produced in oxide of ethyle by the action of chlorine have lately been carefully studied by Malaguti and Regnault, and the facts discovered by them shed light on a multitude of phenomena, the explanation of which had long been sought for in vain. In treating of the production of acetic acid from alcohol, it has been mentioned that by the action of oxygen 2 eq. hydrogen are removed, and replaced by 2 eq. oxygen. The same reaction takes place with chlorine, and a compound is produced, the formula of which is $C_4H_3\left\{\begin{smallmatrix} O \\ Cl_2 \end{smallmatrix}\right\}$. This formula represents anhydrous acetic acid in which 2 eq. oxygen have been replaced by 2 eq. chlorine. When anhydrous ether is saturated with dry chlorine gas, at first with the aid of external cold, afterwards at a gentle heat, a large quantity of hydrochloric acid gas is disengaged, and there is left a colourless oily liquid, which is the above compound, although not quite pure. It may be called *oxychloride of acetyle*. It is contaminated by the presence of a little chloral, and another compound containing chlorine, which seems to be resolved by contact with water into hydrochloric acid and aldehyde. It is kept for some days in contact with water, which is frequently changed, and at last dried in vacuo over sulphuric acid. By these means the pure oxychloride of acetyle alone is left. It forms a neutral, heavy, colourless, oily fluid, of a penetrating odour, like that of oil of fennel. At 284° it boils and is decomposed. Its characteristic property is that of being converted when warmed with water into hydrochloric and acetic acids. This change is instantaneous in contact with alkaline solutions. Sulphuric acid decomposes and blackens it. When heated with potassium, it yields chloride of potassium and a gaseous compound, C_4H_3OCl , containing only half as much chlorine as the original liquid. Compounds of an analogous nature, in which the chlorine is wholly or partially replaced by sulphur, may be obtained by the action of sulphuretted hydrogen gas on the oxychloride. When that gas is passed through the liquid, hydrochloric acid is disengaged, and there is formed an oily, colourless, fœtid liquid, which blackens on exposure to the air, and gradually passes for the most part into a crystalline mass. Hot alcohol dissolves this, and on cooling, deposits tolerably large colourless prisms, fusible between 228° and 235° , not volatile, insoluble in water, soluble in alcohol and ether. The formula of this compound, which may be called oxysulphuret of acetyle,

is $C_4H_3\left\{\begin{smallmatrix} O \\ S_2 \end{smallmatrix}\right\}$, according to which it is anhydrous acetic acid in which 2 eq. oxygen have been replaced by 2 eq. sulphur. In contact with an alcoholic solution of potash, it forms sulphuret of potassium and acetate of potash. The mother-liquid of these crystals, on further evaporation, yields yellow unctuous scales, fusible about 160° , and possessing analogous properties. It is distinguished from the first by containing only 1 at. sulphur, and in the place of the second 1 at.

chlorine. Its formula is $C_4H_3\left\{\begin{smallmatrix} O \\ Cl \\ S \end{smallmatrix}\right\}$. With an alcoholic solution of potash, this body gives sulphuret and chloride of potassium, with acetate of potash.

The compounds of oxide of ethyle (ether) with acids are acted on by chlorine very much as the ether itself, with this difference, that the acids, when not altered by chlorine, and, when they are altered by it, the new substances formed, remain in combination with the oxychloride of acetylene.

Acetic ether gives with it a compound, the formula of which is $C_8H_6O_4Cl_2$. It consists of anhydrous acetic acid and oxychloride of acetylene $= C_4H_3O_3 + C_4H_3\left\{\begin{smallmatrix} O \\ Cl_2 \end{smallmatrix}\right\}$. Oxalic ether gives rise to a number of chlorinised products, which have been investigated by Malaguti. Their true nature and constitution is still very obscure. Benzoic ether, when acted on by chlorine, takes up 3 eq., but gives off only 2 eq. hydrochloric acid; and a substance is formed consisting of 1 at. chloroide of benzoyle, and 1 at. oxychloride of acetylene. $BzCl + C_4H_3\left\{\begin{smallmatrix} O \\ Cl_2 \end{smallmatrix}\right\}$. Here the chloroide of benzoyle has obviously been formed by the action of 1 eq. hydrochloric acid on 1 eq. anhydrous benzoic acid in the nascent state.

When ether is exposed still longer to the action of chlorine, with a gradually increasing temperature, a heavy oily liquid is at last obtained, which is not acted on by water or aqua potassæ. It may be distilled unaltered with oil of vitriol, at least in great part. It boils at 277° , and has the sp. gr. 1.611. In an alcoholic solution of potash it dissolves, chloride of potassium is deposited in abundance, and water separates from the liquid a new oily compound.

If chloroide of ethyle be exposed in a proper apparatus to the action of chlorine gas and the rays of the sun, a violent reaction takes place, with disengagement of hydrochloric acid. A new compound is formed, which has the same composition, and the same density in the state of

vapour, as the so-called oil of olefiant gas. Its smell and some other properties are also very similar, but it is in reality a very different body. It boils at 149° , and may be distilled with potassium or an alcoholic solution of potash without change. Its formula is $C_4H_4Cl_2$; so that it is derived from chloride of ethyle, C_2H_5Cl , in which 1 eq. hydrogen is replaced by 1 eq. chlorine.

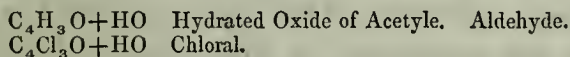
When this compound is exposed to the further action of chlorine and light, a series of remarkable compounds is obtained. The first is a compound of chlorine, analogous to acetic acid, in which all the oxygen is replaced by its equivalent of chlorine.

Formula, $C_4H_3Cl_3$.

It may be called *Chloride of Acetylene*. It boils at 167° . The sp. gr. of its vapour is 4.61. The formula of the next compound is $C_4H_2Cl_4$. It boils at 215° . Its sp. gr. as vapour is 5.79. A third compound is C_4HCl_5 ; and the fourth and last is chloride of carbon, C_4Cl_6 , or $2(C_2Cl_3)$, in which all the hydrogen of ethyle is replaced by chlorine. (Regnault.)

CHLORAL.

By the action of chlorine on alcohol *Chloral* is formed; a substance which represents aldehyde in which the hydrogen of the oxide of acetylene is replaced by chlorine.



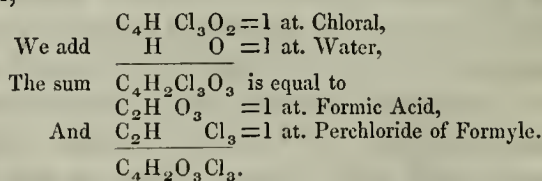
Apparently the effect of chlorine on alcohol is first to form aldehyde, and by the further action of the chlorine on that substance the chloral is formed. But the attempts which have been made to form chloral by the direct action of chlorine on aldehyde have failed, owing to the facility with which aldehyde is converted into a number of different products. Chloral is obtained, but mixed with other compounds of chlorine. Very diluted alcohol yields with chlorine only aldehyde and hydrochloric acid; and an excess of chlorine causes the aldehyde to pass into acetic acid. Alcohol of 80 to 85 p. c. yields with chlorine the so-called heavy muriatic ether. To prepare chloral, anhydrous alcohol is placed in a retort, and dry chlorine is passed through it. At first cold must be applied, but afterwards a gentle heat is required to promote the action. Every bubble produces a flash of light, and a very long time is required to complete the decomposition of only a moderate quantity of alcohol. An enormous quantity of hydrochloric acid is disengaged, which must be sent either up the chimney or out of the window. This is best done by introducing through the neck of the retort into the body a long tube, which is bent upwards

after it leaves the retort, and by which the gas may be conducted away. In this tube, alcohol and chloral, carried off by the gas, are condensed, and flow back into the retort. The chlorine is introduced by a tube passing through the tubulure of the retort. As soon as chlorine, even at the boiling temperature, passes through unchanged, the operation is complete. The liquid generally solidifies on cooling, forming a white crystalline mass, *hydrate of chloral*. It is melted by a gentle heat, and agitated in a stoppered bottle with twice or thrice its volume of oil of vitriol. When the mixture is gently warmed, impure chloral rises to the surface, as a colourless oily stratum. It is removed, and boiled for some time, to expel hydrochloric acid and alcohol; and distilled with its own volume of oil of vitriol. It is finally rectified along with finely powdered quicklime, and the distillation is stopped as soon as the surface of lime is dry. What has passed over is pure chloral.

Formula, $C_4Cl_3O + HO$, or $C_4HCl_3O_2$.

Chloral is a mobile oily liquid, of a peculiar, penetrating, agreeable smell. It causes a flow of tears. Its taste is at first slight and fatty, afterwards acid. Its sp. gr. at 65° is 1.502. It boils at 202° . It is miscible with ether and alcohol, and dissolves sulphur, phosphorus, and iodine. The *hydrate of chloral*, according to Dumas, consists of 1 at. chloral and 2 at. water. When chloral is mixed with water, it at first dissolves, and after some minutes is converted into a semi-solid mass, translucent, and formed of fine needles, soluble in a larger quantity of water, and crystallizing in large rhomboidal crystals by the evaporation of this solution in vacuo over sulphuric acid. The formation of this hydrate, in the preparation of chloral, from anhydrous alcohol depends on the action of the hydrochloric acid produced in the process on a portion of undecomposed alcohol, whereby chloride of ethyle and water are formed. The solution of chloral has the taste and smell of that substance, is neutral, and does not precipitate nitrate of silver.

The dry hydrate may be distilled without change. When heated with caustic alkalis, it is resolved into perchloride of formyle, formiate of the alkali, and chloride of the metal. If to the elements of 1 at. chloral,



The metallic chloride, formed along with the alkaline formiate, is a secondary product of the decomposition of the perchloride of formyle.

The final result appears to be that from 6 at. chloral and 10 at. alkali there are obtained 3 at. metallic chloride, 7 at. alkaline formiate, and 5 at. perchloride of formyle.

Chloral, like aldehyde, cannot be kept without change. After some time it solidifies into a white translucent mass like porcelain, the so-called insoluble chloral. This change takes place equally in close vessels and in the air. There is no disengagement of gas and no gain of weight. This solid body is most readily formed, when alcohol charged with chlorine, as in the preparation of chloral, is mixed with oil of vitriol and allowed to stand in open vessels. The oily stratum swimming over the acid very soon solidifies, and the degree of its solidification furnishes the best test of the progress of the operation. The insoluble chloral appears to be partially decomposed by washing with water. When distilled, it yields chloral, which soon solidifies again. Treated with potash it yields formiate of potash and perchloride of formyle, with chloride of potassium, just as chloral does.

From the mode of its formation, it is probable that this substance differs from chloral, exactly as metaldehyde and elaldehyde do from aldehyde. This has indeed been established by the researches of Regnault, and more recently by those of Städeler, who has also shewn that chloral may be obtained by distilling starch or sugar with hydrochloric acid and peroxide of manganese.

CHLORACETIC ACID.

Discovered by Dumas. Pure hydrated acetic acid is exposed to the combined action of chlorine gas and the sun's rays. After 24 hours the sides of the vessel are covered with crystals, which are dissolved out by a small quantity of water. The solution contains chloracetic acid, with hydrochloric, oxalic, and acetic acids. It is allowed to evaporate in vacuo, over saucers containing oil of vitriol and fused potash. Oxalic acid first crystallizes, then chloracetic acid. The mother-liquid is distilled with anhydrous phosphoric acid, which retains the water, and decomposes the oxalic acid. Acetic acid first passes over, then chloracetic acid in crystals, which are purified by wrapping them in bibulous paper, and leaving them in vacuo for 24 hours. Pure chloracetic acid is left. It forms colourless rhomboidal needles and plates, with a faint smell and a caustic taste, very deliquescent in moist air. It bleaches and corrodes the skin, causing blisters. The vapour of the acid, when heated, is very irritating and suffocating, and very oppressive to the respiratory organs. The solution reddens vegetable blues without bleaching them. The crystals melt at 115° , but

do not again become solid till the temperature falls to 108° . The sp. gr. of the liquid acid at 115° is 1.617. When heated with an excess of potash, this acid undergoes a very striking change. It is resolved into perchloride of formyle and carbonic acid; or we obtain chloride of potassium, formiate of potash, and carbonate of potash.

Formula, $C_4Cl_3O_3 + HO$.

Chloracetic acid combines with bases, its water being replaced by an equivalent of the base; and forms salts which are soluble in water, and possess a remarkable analogy with the acetates. As the acetates are decomposed by digestion with excess of alkali, becoming brown, so also are the chloracetates, only with greater facility.

Chloracetate of Ammonia.—Formula, $C_4Cl_3O_3 + NH_4O + 4 \text{ aq.}$ It is crystallizable; and is decomposed when heated with excess of ammonia, yielding perchloride of formyle and carbonate of ammonia. This is easily explained, as the chloracetic acid contains the elements of 1 at. perchloride of formyle and 2 at. carbonic acid. $C_4Cl_3HO_4 = C_2HCl_3 + 2CO_2$.

Chloracetate of Oxide of Ethyle.—Prepared by distilling a chloracetate, or chloracetic acid, with sulphuric acid and alcohol. Water, added to the product, separates the chloracetic ether in the form of a colourless heavy oil, having an odour similar to that of the so-called heavy muriatic ether. Formula, $C_4Cl_3O_3, AeO$.

Chloracetate of Potash.—Obtained by neutralizing the acid with carbonate of potash, and spontaneous evaporation of the solution, in fine silky crystals, permanent in dry, but deliquescent in moist air. When heated, is decomposed with a feeble explosion. Boiled with excess of potash, it yields a large quantity of formiate of potash.

Formula, $C_4Cl_3O_3, KO + \text{aq.}$

Chloracetate of Silver.—Prepared by dissolving oxide of silver in the acid, and evaporation in vacuo. It forms shining scales or crystalline grains. It is sparingly soluble in water, and explodes when heated. If moistened with alcohol, and set fire to, chloride of silver is left. Formula, $C_4Cl_3O_3, AgO$.

Dumas considers chloracetic acid to be acetic acid in which all the hydrogen of the radical has been replaced by chlorine without affecting the type; and he considers the similarity between its properties and those of acetic acid as a very strong argument in support of this view. But Berzelius denies the similarity of properties, and, rejecting the doctrine of substitutions altogether, considers this acid as formed of oxalic acid and sesquichloride of carbon, $C_2O_3 + C_2Cl_3$, the latter being coupled with the former, without affecting its acid properties.

HEAVY MURIATIC ETHER.

This name has been given to a liquid obtained by Scheele from the distillation of oil of vitriol, chloride of sodium, hyperoxide of manganese, and alcohol; and which is also obtained when alcohol of 80 to 85 p. c. is saturated in the cold with chlorine, then mixed with water, and the oily fluid which separates washed with water as long as any of it is dissolved. These products, which vary much in composition, enter into the constitution of the spiritus muriatico-ethereus, a remedy occasionally used on the Continent. A similar substance is obtained by saturating alcohol with chloride of lime, mixing it with twice its volume of water and distilling it, without separating the oil which is deposited, along with half its weight of hyperoxide of manganese. The product, well washed with water, is the pure ether in question. It boils at from 230° to 250° . Its sp. gr. is 1.227. Heated with aqua potassæ it is decomposed, with disengagement of heat; and a new liquid containing chlorine distils over, which boils at 219° , and has the sp. gr. 1.074. The potash retains a brown resinous matter. The heavy muriatic ether, as first obtained, contains oxychloride of acetylene, and a substance which, by the action of water, is converted into aldehyde and hydrochloric acid; but its composition in the pure state is not known, and the whole subject requires a thorough investigation.

BROMAL.

Discovered by Löwig. Formula, $C_4Br_3O + HO$. It is obtained by the action of bromine on alcohol, and is purified much in the same way as chloral, to which it is quite analogous. It is a colourless oily fluid, of a penetrating odour, which attacks the eyes. It boils above 212° . Sp. gr. 3.34. With caustic alkalies it undergoes the same change as chloral, producing bromide of the metal, perbromide of formyle, and formiate of the alkali. Bromal forms a hydrate with 4 at. water, which readily crystallizes. When bromine is made to act on ether, a variety of compounds is produced, the nature of which has not yet been ascertained.

IODINE AND ALCOHOL.

Iodine is soluble in alcohol, forming a deep brown solution. If this be mixed with an alcoholic solution of potash, it yields iodide of potassium, formiate of potash, and iodide of formyle, in silky yellow crystals. If iodine and alcohol be added to strong nitric acid, as long as the liquid remains colourless, an oily liquid is obtained according

to Johnston, the composition of which is unknown. According to Aimé, if 4 parts of alcohol and 1 of iodine be mixed, and 1 part of fuming nitric acid added, the mixture, being left to itself, deposits an oily liquid, of which likewise nothing certain is known.

Chlorocyan-aldehyde.—Formula, $C_{16}H_{14}O_8N_4Cl_4$. If a current of dry chlorine be passed through a solution of bityanuret of mercury in alcohol, kept as cool as possible, an immense number of crystals make their appearance in the liquid. These consist of a mixture of sal-ammoniac and the aldehyde compound. The crystals are to be thrown upon a filter and washed with cold water, till every trace of sal-ammoniac and cyanuret of mercury is removed. By dissolving them again in alcohol much larger crystals may be obtained. They have a silvery lustre, resembling sulphate of quinine, are neutral, have neither taste nor smell. They melt at 120° , but are partly sublimed before melting. They are insoluble in cold water, but very soluble in alcohol and ether.—Stenhouse. The above empirical formula may be represented as follows: $3(C_4H_4O_2) + 2CyCl + 2HO$; that is, 3 at. aldehyde, 2 at. chloride of cyanogen, and 2 at. water.

The chlorocyanic ether of Aimé is no determinate compound, but consists chiefly of a mixture of light and heavy muriatic ether.

PRODUCTS OF THE DECOMPOSITION OF ALCOHOL, THE CONSTITUTION OF WHICH IS UNCERTAIN.

Hyduret of Acetylene.—Under the name of olefiant gas, a substance has been frequently mentioned in the preceding pages, which is produced as a constant result of the decomposition of alcohol by an excess of sulphuric acid. This substance consists of carbon and hydrogen, equivalent to equivalent. It is distinguished from all other carbo-hydrogens by its tendency to combine as well with simple as with compound bodies. It is named from the fact of its forming an oily compound with chlorine. Berzelius calls it Elayle. But if we examine closely its chemical relations, it appears highly probable that the formula $C_4H_3 + H = C_4H_4$ represents its constitution. This view sheds much light over the cause of its tendency to enter into new combinations, and the phenomena attending the decomposition of its compounds. According to this formula, it is a hyduret of acetylene, corresponding to the oxide of acetylene.

It is obtained in a state of purity, when 1 part of alcohol is heated with 6 or 7 of oil of vitriol. At first ether, then oil of wine, passes over; at last there comes a mixture of equal volumes of sulphurous acid and olefiant gas. It is purified by passing it through milk of lime, which retains the sulphurous acid, and through oil of vitriol, which ab-

sorbs water, ether, and alcohol. Pure hyduret of acetylene has a feeble ethereal odour; it burns with a white and very luminous flame. In contact with chlorine, equal volumes of the two gases condense into an oily fluid, the hydrochlorate of chloride of acetylene, or the oil of the Dutch chemists. Olefiant gas combines with bromine, iodine, and anhydrous sulphuric acid. When 1 vol. of this gas and 2 vol. chlorine are quickly mixed in an open cylinder, and a burning body approached to the mixture, combustion takes place with a red flame, without explosion; hydrochloric acid is formed, and carbon is deposited in thick black flocculi.

Chloride of Acetylene.—When the oil above mentioned (hydrochlorate of chloride of acetylene) is left for some days in contact with an alcoholic solution of potash, the hydrochloric acid is destroyed, producing water and chloride of potassium, and there is left protochloride of acetylene, which is dissolved by the alcohol. A gentle heat disengages it in the form of gas, along with the vapours of alcohol and water. The gas is purified by being passed through oil of vitriol. Protochloride of acetylene is gaseous at the ordinary temperature, has an alliaceous smell, burns with a dark red flame fringed with green; its sp. gr. in the state of gas is 2.166. At 0° it condenses into a liquid. Potassium, heated in the gas, decomposes it, producing chloride of potassium, naphthalene, and carbon. Formula, C_4H_3Cl .

If this gas be passed through the perchloride of antimony, it is entirely absorbed. The addition of water separates a liquid, which is a mixture of the oil of olefiant gas with another compound, which has the empirical formula $C_4H_3Cl_3$, and might be considered, like the compound mentioned (p. 925), as acetic acid in which the oxygen is replaced by chlorine; but, from the phenomena of its decomposition by potash, its real formula must be $C_4H_2Cl_2 + HCl$. When the above mixture is distilled, the oil of olefiant gas passes over, till the temperature rises to 235° ; after which the new compound passes over pure. It is fluid, colourless, of sp. gr. 1.422 in the liquid form: in the form of vapour, 4.75. When it is distilled with an alcoholic solution of potash, it produces chloride of potassium, water, and a new substance, boiling at 86° , the formula of which is $C_4H_2Cl_2$. Its density in the form of vapour is 3.34. If we take the half of the above formula, C_2HCl , this substance would seem to be the protochloride of formyle, the radical of formic acid. This name has been given to it by Regnault, who discovered it.

Perchloride of Acetylene.—This is the compound corresponding to acetic acid, which Regnault obtained by the action of chlorine on the chloride of ethylene with the aid of the sun's rays.

Formula, $C_4H_3Cl_3$. (See p. 925.)

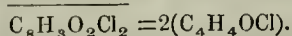
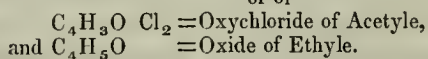
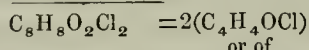
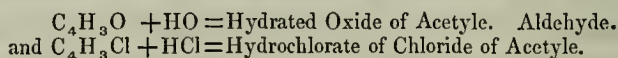
Protobromide of Acetylene.—Prepared as the protochloride, only using the corresponding compound of bromine. It is gaseous, has an alliaceous smell. Its sp. gr. in the form of gas is 3.691.

Formula, C_4H_3Br .

Hydrochlorate of Chloride of Acetylene. *Syn. Oil of Olefant Gas; Oil of the Dutch Chemists*.—Discovered by Deimann, Troostwyk, Lauwerenburgh, and Vrolich. It is commonly prepared by mixing moist chlorine and olefant gases in equal volumes; but it is preferable to pass olefant gas into perchloride of antimony as long as it is absorbed. The saturated fluid is distilled, when the oil in question passes over. It is purified by repeated rectification with oil of vitriol, and washing with water, and is dried by means of chloride of calcium.

It is a colourless mobile liquid, of an agreeable ethereal odour and a sweet taste. It boils at 180° . The sp. gr. of its vapour is 3.4484. It is not altered by distillation with oil of vitriol or with caustic potash. It burns with a luminous flame edged with green, and smoky. It communicates to water its smell, without being perceptibly dissolved; and it is miscible in all proportions with alcohol and ether. When mixed with an alcoholic solution of potash, it is gradually decomposed, yielding chloride of potassium and protochloride of acetylene. It absorbs chlorine, producing hydrochloric acid, and other compounds richer in chlorine. Among these are the compound already mentioned, $C_4H_2Cl_2 + HCl$; and another, $C_4H_2Cl_4$, or $C_2H + Cl_2$, which may be considered as the deutochloride of formyle. When all the hydrogen is replaced by chlorine, which happens after long exposure to the combined action of light and chlorine, there is obtained sesquichloride of carbon, $C_4Cl_6 = 2(C_2Cl_3)$.

Under the name of Chloretal, D'Arcet has described a substance produced by the action of chlorine on impure olefant gas, containing the vapours of alcohol and ether. When the oil so obtained is rectified till the temperature rises to 365° , this substance then passes over. It is a colourless liquid of a peculiar odour, different from that of the oil of olefant gas. It is decomposed by water, alkalis, and sulphuric acid. According to D'Arcet, its formula is C_4H_4OCl ; so that it may be a compound of



This substance is worthy of more minute investigation.

Hydrobromate of Bromide of Acetylene.—Discovered by Serullas. Prepared by the action of bromine on olefiant gas. In its formation, its purification, and properties, it is very analogous to the corresponding compound of chlorine already described. Sp. gr. at 70° , 2.164. It boils at about 265° , and solidifies at 5° .

Formula, $C_4H_3Br + HBr$.

Hydriodate of Iodide of Acetylene.—When iodine is exposed to the action of olefiant gas, a solid compound is obtained, heavier than oil of vitriol, fusible at 175° , and forming a crystalline mass on cooling. It is decomposed by chlorine and bromine. It is uncertain, from the weaker affinities of iodine, whether it be really a compound analogous to the two preceding, $C_4H_3I + HI$; or whether its more probable formula be not $(C_4H_3)H + I_2$, that is, a compound of hyduret of acetylene (olefiant gas) with iodine.

Hyposulpho-acetylic Acid, or Quadrisulphate of Hyduret of Acetylene.—Discovered by Regnault. Olefiant gas is absorbed by anhydrous sulphuric acid, with production of heat, and without blackening. The acid ceases to fume on exposure to the air, and is converted into a white crystalline body, which is fusible at 175° , and may be sublimed. When dissolved in water, it takes up 1 at. water, and forms hydrated ethionie acid. (See Ethionie Acid.) It absorbs ammonia; and, when the compound is gently heated, it is decomposed with explosion, and converted into a black mass. Formula, $4SO_3 + C_4H_3, H$.

Chloride of Platinum and Acetylene.—This compound was first noticed by Berzelius, but has been minutely studied by Zeise. It is produced by the action of chloride of platinum on alcohol, along with aldehyde and chloride of ethylene. It appears most probable that the oxide of ethylene of the alcohol is resolved, as in so many decompositions, into water and hyduret of acetylene (olefiant gas); and that the latter, with chloride of platinum, produces the new double chloride, hydrochloric acid, and free chlorine. By the action of the hydrochloric acid on the alcohol, chloride of ethylene is formed; and by the action of chlorine on alcohol, aldehyde also is produced. Three at. oxide of ethylene, with 4 at. bichloride of platinum, produce 1 at. aldehyde, 1 at. water, 2 at. chloride of platinum and acetylene, and 4 at. hydrochloric acid: if this be the true explanation, the formula of the double chloride will be $(C_4H_3)Cl + Pt_2Cl$. It will then correspond to the oil of olefiant gas, $(C_4H_3)Cl + HCl$; one atom of hydrogen being replaced by two of platinum. According to Zeise, the formula is $C_4H_4Pt_2Cl_2$, or $(C_4H_3)H + Pt_2Cl_2$. In this case 2 at. oxide of ethylene with 2 at. bichloride of platinum would form 1 at. of the new compound, 1 at. aldehyde, and 2 at. hydrochloric acid. Malaguti considers the salt in question is a

compound of oxide of acetylene with chloride of platinum = $(C_4H_3)O + Pt_2Cl_2$. But Zeise's experiments seem to demonstrate the absence of oxygen in the compound; and, besides, it is not easy to see how the chloride of platinum could act on the ether so as to yield Malaguti's formula, along with aldehyde and the other products. On this view 1 at. oxide of ethylene should act on 2 at. bichloride of platinum, and the only products should be the double chloride and hydrochloric acid.

The double chloride itself is obtained pure by adding to the solution of the compound it forms with chloride of potassium, or with sal-ammoniac, bichloride of platinum as long as it causes a precipitate, and evaporating the filtered liquid in vacuo over sulphuric acid in a dark place. It forms a transparent honey-yellow mass, which is blackened by light. It is very prone to decomposition. The solution of bichloride of platinum in alcohol always contains a little of this compound. It is soluble in alcohol, and a thin film of this solution, dried on the surface of glass or porcelain, and heated red-hot, leaves a brilliant surface of platinum, which adheres very firmly.

The solution of the chloride of platinum and acetylene, when digested with hydrate of magnesia, gives chloride of magnesium, which is dissolved, and a slimy greyish brown precipitate, which gradually becomes dense and black. When the excess of magnesia is dissolved out by nitric acid, there remains a black powder, which, if dried and heated, explodes, leaving platinum. It is possible that this may be a compound of acetylene with 2 at. suboxide of platinum, or of a compound of platinum and acetylene with oxide of platinum. The same substance, although probably containing more platinum, is formed by digesting alcohol with subchloride of platinum. This powder also explodes when heated, and possesses in a high degree the power of absorbing oxygen, converting alcohol into acetic acid, &c.

Triple Chloride of Potassium, Platinum, and Acetylene.—Pure bichloride of platinum is dissolved in alcohol with a little hydrochloric acid and one-eighth of its weight of chloride of potassium, and digested at a boiling heat for some time. The alcohol is distilled off, and the residue saturated with carbonate of potash, and evaporated by a gentle heat till it crystallizes. It forms lemon-yellow, regular translucent prisms, which at 212° lose 2 at. water. It is soluble in water, especially if hot; and in alcohol. The solution is decomposed by heat, with the separation of metallic platinum. It is decomposed by the action of light, and of chlorine and hydrogen, when heated in those gases.

Formula, $(C_4H_3)Cl + Pt_2Cl + KCl$.

Similar triple chlorides may be obtained with chloride of sodium and

chloride of ammonium (sal-ammoniac). In properties and composition they resemble the salt just described.

When the solution of either of these salts is mixed with ammonia, a lemon-yellow precipitate is obtained, the formula of which is $(C_4H_3)Cl + P_2Cl + NH_3$. It is sparingly soluble in water, soluble in alcohol. It is decomposed by light and heat. Potash disengages ammonia from it.

PRODUCTS OF THE DECOMPOSITION OF ACETIC ACID AND THE ACETATES.

1. *Acetone, its Compounds, and the Products of its Decomposition.*—When the vapour of hydrated acetic acid is passed through a red-hot tube, it is entirely resolved, without deposition of carbon, into a volatile liquid, acetone, and a mixture of carburetted hydrogen, carbonic oxide, and carbonic acid gases. If the heat go beyond a dull red, the acid is resolved into a brown oil and inflammable gases, with deposition of carbon.

Acetates, the bases of which retain carbonic acid at a red heat, produce, when heated in close vessels, the carbonate of the base and acetone. This takes place, for example, with the acetates of potash, soda, and baryta. Where the oxide cannot retain carbonic acid at a red heat, as in the case of acetates of magnesia, zinc, or manganese, the acetone is accompanied by carbonic acid. If the oxide be easily reducible, as in the acetates of copper, silver, and mercury, there are given off hydrated acetic acid, carbonic oxide, carbonic acid, water, and acetone, and there is left a mixture of the metal with carbon in a minute state of division.

Neutral acetate of lead, melted at 365° , solidifies after a time into a white crystalline frothy mass of sesquibasic acetate of lead, while one-third of the acetic acid is expelled in the form of carbonic acid and acetone. The formula of acetone is C_3H_3O . If to this we add the elements of 1 at. carbonic acid, the result is 1 at. anhydrous acetic acid, $C_3H_3O + CO_2 = C_4H_3O_3$. This explains sufficiently all the above reactions.

Acetone.—The liquid obtained by passing acetic acid through a red-hot tube, or by distilling the acetate of lime, is rectified over quicklime in the water-bath till its boiling point becomes constant. It then forms a clear colourless liquid, of a peculiar, penetrating, somewhat empyreumatic smell. Its sp. gr. is 0.7922 in the liquid form; 2.022 in the form of vapour. It boils at 132° . Acetone has a pungent taste, resembling that of peppermint; and is miscible with water, alco-

hol, and ether in all proportions. In contact with caustic alkalies and air, acetone absorbs oxygen, and produces, among other products not examined, a brown resinous substance. Heated with chloride of lime, it yields carbonic acid and chloride of formyle. It is also decomposed by chlorine and oil of vitriol. It is inflammable, and burns with a luminous flame.

Its formula is C_3H_3O .

In the preparation of acetone there is obtained, in variable quantity, an oily liquid, much less volatile than acetone, which remains in the retort when the impure acetone is rectified. It has a disagreeable smell and a burning taste, boils at 248° ; the sp. gr. of its vapour is 5.204 . Its formula is $C_{10}H_8O$. Kane, who described and analysed this oil, has given it the name of *Dumasine*, out of compliment to M. Dumas. It is to be hoped that this principle of nomenclature may not be followed in chemistry.

The chemical nature and constitution of acetone are still doubtful. It contains the elements of 1 at. carbonate of oxide of ethyle and 1 at. hyduret of acetylene $= C_9H_9O_3$; or of 1 at. acetate of oxide of ethyle and 1 at. hyduret of acetylene $= C_{12}H_{12}O_4$. According to Kane, it has a constitution similar to that of alcohol, and is the hydrate of the oxide of an organic radical, $C_6H_5 = (C_6H_5)O + HO = C_6H_6O_2$. This radical he calls *Mesityle*.

By distilling acetone with fuming sulphuric acid, Kane obtained, along with a number of other products, a substance, the formula of which he states to be C_6H_4 . (His analysis rather leads to the formula $C_{12}H_9$.) To this substance he has given the name of *Mesitylene*.

By the action of perchloride of phosphorus on acetone, Kane obtained a compound C_6H_5Cl , *chloride of mesityle*, which, by the action of aqua potassæ, yielded chloride of potassium and the compound C_6H_5O , *oxide of mesityle*, differing from acetone as ether does from alcohol, namely, by 1 at. of water. By saturating a mixture of acetone and fuming sulphuric acid with lime and other bases, peculiar salts were obtained, containing the elements of sulphuric acid, oxide of mesityle, and a metallic oxide. These salts, according to Kane, are analogous to the sulphovinates (double sulphates of oxide of ethyle and bases); but the theoretical views of Kane concerning these compounds do not appear to express their true nature.

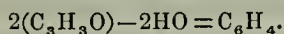
That view which considers alcohol as the hydrate of an organic oxide of basic properties derives its chief support from the fact, that the oxide of ethyle, when separated from its compounds, possesses the property of combining with water, and reproducing alcohol. But we cannot reproduce acetone from any of the compounds described by

Kane, and which, according to him, contain the oxide of mesityle. Ether (oxide of ethyle) is an oxide, because it combines with acids, atom to atom. It also forms double salts, in which one atom of acid is neutralized by the ether, another by a metallic oxide. Now, neither acetone nor oxide of mesityle form similar compounds. In the compound of Kane's oxide of mesityle with sulphuric acid, the acid retains its capacity of saturation unimpaired, and 2 atoms of sulphuric acid neutralize 2 at. metallic oxide. Consequently, the oxide of mesityle does not exist in this compound as a base, but in the same state as the coupled body or conjunct in those coupled or conjugate acids which are now so numerous; in the state, for example, of the benzoic acid in the hyposulphobenzoic acid. Moreover, Frémy has described a substance, *Metacetone*, which has the same composition as Kane's oxide of mesityle, but very different properties. We know nothing of the real relation between these two substances and acetone.

Without, therefore, adopting Kane's theoretical views, we shall briefly describe the substances formed by him, under the names he has given them.

Mesitylene.—Formula, C_6H_4 . (Kane, Plantamour.) To prepare it, acetone is distilled with half its volume of fuming sulphuric acid. On the surface of the distilled liquid swims a yellowish oil, which is washed with water and then rectified. As it sometimes contains acetone, it is again heated in the water-bath, which expels the acetone. Mesitylene, when pure, boils at 275° . When the temperature, during the rectifications, rises higher than this, it is owing to the presence of another substance, resembling mesitylene, but less volatile.

Mesitylene is an oily, colourless liquid. It has a faint and somewhat alliaceous smell.* It is lighter than water, inflammable, and burns with a white smoky flame. Alkalies do not act on it. Sulphuric acid, nitric acid, and chlorine act on it as they do on benzole. According to its formula, it contains the elements of 2 at. acetone, minus 2 water, which explains its formation.



Oxide of Mesityle.—Formula, C_6H_5O . (Kane.) Obtained by acting on an alcoholic solution of chloride of mesityle by caustic potash in excess, and then adding a large quantity of water. An oily liquid separates, which is decanted, dried by contact with chloride of calcium, and rectified. It is a colourless liquid, having an odour like that of

* By the action of sulphuric acid on the less volatile portion of the products of the distillation of caoutchouc, I obtained an oil, which in all external properties was identical with Kane's mesitylene—W. G.

peppermint. It boils at 248° , is inflammable, and burns with a very brilliant flame and much smoke.

Chloride of Mesityle.—This compound cannot be obtained by the action of hydrochloric acid either on acetone or on the preceding substance. Its formula, according to Kane, is C_6H_5Cl ; but, of several analyses, one only gave results approximating to theory. Its composition cannot therefore be considered as fully ascertained. To obtain it, 2 parts of perchloride of phosphorus are added by degrees to 1 part of acetone, the mixture being surrounded by cold water. On adding water, the chloride of mesityle separates as an oily liquid, heavier than water. Heat converts it into hydrochloric acid and mesitylene, so that it would seem that the chlorine in this compound cannot be replaced by oxygen.

Iodide of Mesityle is obtained by the distillation of a mixture of iodine, phosphorus, and acetone; but never in a state of purity. It seems to be analogous to the chloride. The residue of the distillation contains hypophospho-mesitylous acid, and another compound containing iodine, in golden-yellow scales, which Kane calls Iodide of pteyle. (See below, p. 941.)

Chloroplatinate of Oxide of Mesityle.—Discovered by Zeise, who called it *Metacechlorplatin*.

Formula, $C_6H_5O + PtCl$.

This is a substance obtained by the action of bichloride of platinum on acetone. When distilled together, hydrochloric acid and an ethereal liquid pass over, and there remains in the retort the new substance mixed with a resinous matter, to which Zeise has given the name of *Resin of platinum*. The chloroplatinate is purified by repeated crystallizations, first in acetone acidulated with hydrochloric acid, afterwards in pure acetone. It forms small yellow crystals, not altered by a heat of 212° , but decomposed by a higher temperature, when it burns with a green flame, and leaves white metallic platinum. It is sparingly soluble in water and alcohol, insoluble in ether. When the mother-liquid of these crystals is heated, gas is disengaged, and a flocculent black powder is deposited, which explodes when heated. Zeise calls it *Pyracechlorplatin*.

Sulphomesitylic Acid.—Formula, according to Kane, C_3H_3O, HO, SO_3 . This acid has not been obtained in a separate state. When its salts are decomposed with this view a liquid is obtained, which blackens on being evaporated, and is then found to contain free sulphuric acid, while it has the odour of sulphurous acid and oxide of mesityle.

Sulphomesitylate of Lime.—Formula, C_3H_3O, CaO, SO_3 . Obtained by neutralizing with lime a mixture of one part of acetone and 2 parts

of fuming sulphuric acid, and filtering to separate sulphate of lime. It is very soluble, deliquescent, and when heated takes fire, and leaves a residue of sulphate of lime.

Sulphomesitylate of Baryta.—Formula, C_3H_3O, BaO, SO_3 . Obtained as the preceding salt. It forms pearly tables, and leaves sulphate of baryta when heated.

When 2 parts of acetone and 1 of sulphuric acid are mixed, and the mixture neutralized with lime, a new salt of lime is obtained, containing twice as much acetone for the same weight of lime and sulphuric acid.

Formula, $C_6H_6O_2, CaO, SO_3$.

Nitric Acid and Acetone.—When 1 part of fuming nitric acid is mixed with 2 of acetone, a violent reaction takes place. When the mixture has cooled, the addition of water causes the separation of a yellow oil, which consists of two different liquids. One of these is viscid, the other very fluid. The former predominates when the action has been very violent, the latter when it has been more moderate. Kane has given to the former the name of *Mesitic aldehyde*; to the latter, that of *Nitrite of oxide of pteleyle*.

Nitrite of Oxide of Pteleyle.—Formula, C_6H_3O, NO_3 . It is heavier than water, and is decomposed by that liquid. Paper impregnated with it burns like tinder. It withstands a heat of 212° ; but cannot be distilled without decomposition. When heated in a tube over the spirit-lamp, it explodes violently.

Mesitic Aldehyde.—Formula, $C_6H_4O_2$. Prepared as above, or by boiling mesitylene in nitric acid as long as reaction is perceived. It is a heavy, viscid, reddish-yellow liquid, of a sweetish penetrating smell. It is very soluble in alkalis, with a brown colour. It absorbs dry ammonia, and forms with it a brown resinoid mass, which is soluble in water, and may be crystallized by careful evaporation. When the liquid is rendered slightly alkaline by potash, nitrate of silver causes in it a precipitate, which, when heated in the liquid, is reduced to the metallic state. Kane considers this as a proof of the analogy of this substance to aldehyde; but the same effect is produced, in the same circumstances, by all soluble organic matters which are not acid. According to Kane, mesitic aldehyde is produced by the direct oxidation of mesitylene by the nitric acid.

Phosphomesitylic Acid.—Glacial phosphoric acid (metaphosphoric acid) is dissolved by acetone, with disengagement of heat, and production of a brown colour. When the mixture is neutralized by bases, soluble salts are obtained.

The salt of soda crystallizes in rhomboidal tables, which effloresce in the air; and, when heated, become first white, then black, and finally

leave a residue of 48.8 p. c. phosphate (pyrophosphate?) of soda. (Kane.)

Hypophospho-mesitylous Acid.—The residue of the distillation of a mixture of iodine, phosphorus, and acetone on cooling forms a mass like asbestos. Water dissolves one portion of the mass, leaving another in yellow scales undissolved. The solution has a taste both acid and bitter. When neutralized with baryta, it forms an insoluble and a soluble salt. The latter forms a crystalline mass when its solution is evaporated. This mass contains iodide of barium and hypophospho-mesitylite of baryta. Boiling alcohol dissolves the iodide of barium, and leaves the new salt, which has now become insoluble in water, and forms small crystalline grains. When heated, they burn with the flame of phosphorus, leaving a black residue, which by calcination is converted into phosphate of baryta. Nitric acid acts violently on this salt with the aid of heat. Formula of the hypophospho-mesitylite of baryta, according to Kane, $C_6H_6O_3P_2, BaO$. But he obtained by the action of nitric acid on it, 74 to 75 p. c. phosphate of baryta, indicating not 2 at. phosphorus to 1 at. baryta, as in his formula, but 3 at. phosphorus to 2 at. baryta. Plantamour could not succeed in obtaining this salt by Kane's process.

ACTION OF CHLORINE AND IODINE ON ACETONE AND MESITYLENE.

Mesitic Chloral.—Formula, $C_6H_4Cl_2O_2$. (Dumas; Kane.) When dry chlorine gas is passed through acetone till all disengagement of hydrochloric acid has ceased, there is obtained a liquid insoluble in water, of a penetrating and offensive odour. Its sp. gr. is 1.33. It boils at 260°; causes blisters on the skin; and when boiled is decomposed with disengagement of hydrochloric acid. It is not acted on by alkalis, nor by oil of vitriol, at the ordinary temperature; but an excess of caustic potash, with the aid of heat, dissolves it, producing chloride of potassium and a new acid, the salts of which are soluble, which has not been particularly examined. The analyses made by Dumas and Kane agree in leading to the above formula; but an analysis by Liebig gave less hydrogen, with more chlorine and oxygen.

Chloride of Pteleyle.—Formula, C_6H_3Cl . (Kane.) Formed by passing chlorine through mesitylene. It separates in crystals, which are purified by solution in ether. When pure, it resembles commercial sulphate of quinine, and is insoluble in water. The analysis of this body also gave results not exactly agreeing with the formula. It

is remarkable that chlorine and nitric acid act differently on mesitylene.

Iodide of Pteyle.—This name has been given by Kane to the yellow scaly crystals obtained in the residue of the distillation of a mixture of iodine, phosphorus, and acetone. They resemble iodoforme (iodide of formyle) in their properties, except that they are volatile in a high temperature without decomposition. Their composition has not been ascertained.

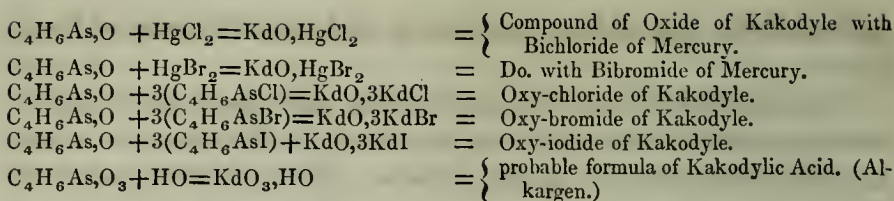
The formulæ which have been given for the compounds just treated of, as products of the decomposition of acetone, must be considered as the expression of a theoretical view, founded on a supposed analogy between acetone and alcohol. Before we can come to any certain conclusions in regard to these compounds, they must all be subjected to a rigid investigation.

COMPOUNDS CONTAINING ARSENIC, DERIVED FROM ACETYLE.

When acetate of potash, mixed with its own weight of arsenious acid, is subject to dry distillation, a liquid is obtained, which was discovered by Cadet, and has long been known under the name of Cadet's fuming liquor. Bunsen has lately studied this substance minutely, and has named it *Alkarsine*, or more systematically oxide of kakodyle. It is characterized by its insupportable smell, and a high degree of spontaneous combustibility. The first analyses of this substance, by Dumas and Bunsen, left it doubtful whether its true formula was C_4H_6As , or, according to the view of Berzelius, C_4H_6AsO ; but the later analyses of Bunsen have decidedly established the latter formula; and his subsequent researches have confirmed the view, first started by Berzelius, that alkarsine is the oxide of a compound radical, *Kakodyle*, (from *κακός*, bad, and *ὀδῶδη*, smell,) the formula of which is C_4H_6As , and its symbol Kd.

The following table contains the compounds of this radical already described and analysed by Bunsen. Only the results, however, are here stated; for the details the reader is referred to the Memoirs of Bunsen published in the *Annalen der Chemie und Pharmacie*.

C_4H_6As	= Kd	= Kakodyle.
C_4H_6As, O	= Kd O	= Oxide of Kakodyle. (Alkarsine.)
C_4H_6As, S	= Kd S	= Sulphuret of Kakodyle.
C_4H_6As, Se	= Kd Se	= Seleniuret of Kakodyle.
C_4H_6As, Cy	= Kd Cy	= Cyanide of Kakodyle.
C_4H_6As, Cl	= Kd Cl	= Chloride of Kakodyle.
C_4H_6As, Br	= Kd Br	= Bromide of Kakodyle.
C_4H_6As, I	= Kd I	= Iodide of Kakodyle.
C_4H_6As, F	= Kd F	= Fluoride of Kakodyle.
$C_4H_6As, Cl + HO$	= KdCl, HO	= Hydrated Chloride of Kakodyle.



It will at once be seen, that the radical may be traced unchanged throughout all these combinations. In fact, it is exceedingly permanent, and has very strong affinities.

Kakodyle.—This compound is best obtained by heating the chloride of kakodyle with zinc, when the zinc seizes the chlorine, displacing the kakodyle. $KdCl + Zn = ZnCl + Kd$. The chloride of zinc is removed by water, which leaves the kakodyle as a liquid, boiling about 338° , of a penetrating garlic odour, instantly bursting into flame on contact with the air. At 21° it forms large square prisms.

In all its chemical relations, it acts as a metal; and were it not that it is destitute of metallic lustre, it might be called a compound metal. With oxygen it forms the oxide of kakodyle, KdO , and kakodylic acid, KdO_3 . With chlorine, bromine, iodine, sulphur, and cyanogen, it also combines directly, yielding the compounds $KdCl$, $KdBr$, KdI , KdS , $KdCy$; all of which may also be formed by the action of the oxide on the respective hydrogen acids of these elements. From its compounds it is displaced by metals, such as zinc, iron, and tin. In short, the whole of its characters are those of an elementary body, or, as Bunsen calls it an organic element, although we know it to be a compound, its formula being $C_4H_6As = Kd$. It is entirely analogous to cyanogen in this respect, except that while cyanogen exhibits the characters of a non-metallic element, kakodyle exhibits those of a metal, not indeed in its outward properties, but in all its affinities and reactions. Cyanogen may be compared to chlorine, kakodyle to potassium or lead.

The existence of kakodyle is of the utmost importance, as proving the existence of compound organic radicals, and their entire analogy, in every point, to elementary bodies. The facts known with reference to kakodyle, along with those connected with cyanogen, admit, in the present state of our knowledge, of but one interpretation; and although the greater number of the organic radicals which we are disposed to admit are not known, as these two are, in the separate state, capable of producing directly all their compounds, yet when we see the analogy presented by the oxides of these hypothetical radicals, particularly in their relations to hydrogen acids, to cyanogen and kakodyle, we must admit the great probability of their existence; and we must

attribute the difficulty or impossibility of obtaining them in a separate form to the natural proneness to decomposition which must belong to such compounds, containing, as they generally do, a large number of elementary atoms in their equivalent molecules. Viewed in this light, the discovery of kakodyle by Bunsen is one of the most important of modern times; and the whole investigation, which established first the existence of the oxide, then that of the other compounds of kakodyle, and, lastly, that of the radical itself, with its striking analogies, will long serve as a model of chemical research. It is impossible to estimate too highly the ability displayed in these researches of Bunsen, which can only be equalled by the patience and perseverance with which he pursued the study of substances so offensive and even dangerous; the mere preparation of which, from their poisonous nature and spontaneous inflammability, as well as from their ready alteration by contact with air, was a matter of the greatest difficulty and delicacy.

Oxide of Kakodyle. Syn. Alkarsine.—Formula, $C_4H_6AsO = KdO$.

Equal weights of acetate of potash and arsenious acid are slowly heated to redness in a glass retort placed in a sand-bath, and connected with a receiver surrounded with ice. Carbonic acid and some inflammable gases are disengaged, metallic arsenic sublimes; and in the receiver are found, besides the metal, two liquids, the heavier of which contains oxide of kakodyle and another heavy arseniuretted compound, while the lighter is a solution of oxide of kakodyle in water, acetone, and acetic acid. From 1 lb. of arsenious acid about 5 oz. of impure oxide of kakodyle are obtained. To purify it, the heavy liquid is agitated with water, to remove acetone or acetic acid, and rectified with caustic potash in an atmosphere of carbonic acid gas. A final rectification over lime or baryta renders it anhydrous.

Oxide of kakodyle is a colourless ethereal liquid, refracting light powerfully, boiling at about 300° ; at -10° congealing into white silky scales. The sp. gr. of its vapour by experiment was found = 7.555. The calculated sp. gr. is 7.828, according to the above formula, C_4H_6AsO .

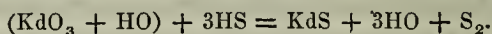
The smell of oxide of kakodyle resembles that of arseniuretted hydrogen, and is in the highest degree offensive. Its vapour irritates the eyes, causing a flow of tears. The liquid, if placed on the skin, causes violent itching. It is a powerful poison in every shape.

Oxide of kakodyle is a feeble base, and combines with acids. With phosphoric and diluted nitric acids it forms viscid liquids; the latter compound produces, in metallic solutions, precipitates not yet exa-

mined. With sulphuric acid, oxide of kakodyle forms white needles, of a very offensive odour, and deliquescent in the air. It is rapidly oxidized by strong nitric acid, chlorine, and bromine, with the production of a new body, kakodylic acid, or alkargen. It absorbs oxygen from the atmosphere, even under water, and is converted into the same compound. When air or oxygen is freely admitted to it, it inflames spontaneously, burning with a pale flame, and forming thick fumes of arsenious acid. It is sparingly soluble in water, miscible in every proportion with alcohol and ether. Oxide of kakodyle is acted on by the hydrogen acids as a metallic oxide is, producing water, and a compound of kakodyle with the radical of the acid : $\text{KdO} + \text{HR} = \text{KdR} + \text{HO}$.

The production of oxide of kakodyle from acetone is very easily explained : 2 at. acetone $\text{C}_6\text{H}_6\text{O}_2$ + 1 at. arsenious acid AsO_3 yield 1 at. oxide of kakodyle, $\text{C}_4\text{H}_6\text{AsO}$ + 2 at. carbonic acid, C_2O_4 .

Sulphuret of Kakodyle.—Formula, $\text{C}_4\text{H}_6\text{AsS} = \text{KdS}$. Formed by distilling chloride of kakodyle with hydrosulphuret of sulphuret of barium. $\text{KdCl} + \text{BaS,HS} = \text{KdS} + \text{BaCl} + \text{HS}$. The sulphuretted hydrogen is disengaged as gas, and its presence is useful in preventing the oxidation of the sulphuret by the atmosphere. It is also formed when oxide of kakodyle is acted on by the same salt, especially if an acid be present ; and, finally, it is produced when sulphuretted hydrogen acts on kakodylic acid, (alkargen,) $\text{KdO}_3 + \text{HO}$.



Here two-thirds of the sulphur are set free.

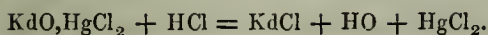
It is a clear liquid, of a most disagreeable smell, nearly insoluble in water, and heavier than that liquid.

Seleniuret of Kakodyle.—Formula, $\text{C}_4\text{H}_6\text{As,Se} = \text{KdSc}$. Very analogous to the sulphuret, both in smell and in other properties.

Cyanide of Kakodyle.—Formula, $\text{C}_4\text{H}_6\text{As,Cy} = \text{KdCy}$. This compound is best formed by distilling a strong solution of bicyanide of mercury along with oxide of kakodyle. Metallic mercury is deposited, part of the oxide is converted into kakodylic acid, and on applying heat, the cyanide distils over. When pure, it forms large brilliant crystals, easily fusible and volatile. Like all these compounds, it has a most offensive smell, and is poisonous in the highest degree. The vapour, in small quantity, causes vomiting, numbness of the extremities, fainting, and other alarming symptoms ; and the utmost caution is required in experimenting on it.

Chloride of Kakodyle.—Formula, $\text{C}_4\text{H}_6\text{As,Cl} = \text{KdCl}$. It is best prepared by distilling the compound of oxide of kakodyle and bichlo-

ride of mercury mentioned in the table, with very strong hydrochloric acid.



It forms a clear liquid, very inflammable, exploding when heated in oxygen gas, and inflaming spontaneously in chlorine gas. It has a most powerful, offensive, and irritating odour, causing violent inflammation of the mucous membrane of the nose, and smarting the eyes very severely. It is also highly poisonous, and great caution is necessary in preparing it.

When exposed to the atmosphere, it deposits crystals, which Bunsen has found to be oxychloride of kakodyle.

Iodide of Kakodyle.—Formula, $\text{C}_4\text{H}_6\text{AsI} = \text{KdI}$.

Its preparation and properties are analogous to those of the chloride.

The *bromide* and *fluoride* of kakodyle are analogous to the two preceding compounds.

The chloride, bromide, and iodide of kakodyle in contact with water form each a basic compound, containing 1 at. oxide of kakodyle and 3 at. of the chloride, bromide, or iodide of kakodyle. The same compounds may be formed by the action of the corresponding hydracids, dissolved in water, on the oxide of kakodyle.

These compounds are liquids, similar in most of their properties to the chloride, bromide, and iodide of kakodyle. Their formulæ have been given in the table.

The compounds of oxide of kakodyle with bichloride and bibromide of mercury are both white crystalline compounds. They are very interesting in reference to the theory of organic compounds, but we have not space here to do more than mention them. Their formulæ, according to Bunsen, will be found in the table. There are many other similar compounds, and also some consisting of chloride of kakodyle with metallic chlorides, as, for example, the double chloride of copper and kakodyle, $\text{KdCl} + \text{CuCl}$.

Kakodylic Acid. *Syn. Alkargen*.—This compound is formed by the oxidation of the oxide of kakodyle. Its formula is $\text{C}_4\text{H}_6\text{AsO}_3 = \text{KdO}_3$.

Air or oxygen is allowed very gradually to come in contact with alkarsine, or impure oxide of kakodyle. At first cold is applied to moderate the combustion. There are formed kakodylic acid, which crystallizes; arsenious acid; and an ethereal volatile product, soluble in water, of an intolerably fœtid smell, *hydrarsine*. Towards the end of the combustion the liquid forms a semi-solid mass, which is acted on by cold water. This dissolves kakodylic acid and hydrarsine, leaving

the greater part of the arsenious acid undissolved. The solution is now evaporated till it forms a solid mass, which is pressed in bibulous paper to remove the hydrarsine. The pressed mass is dissolved in boiling absolute alcohol, which on cooling deposits crystals. These are again pressed in paper, and purified by repeated solution in alcohol, or repeated evaporation of the aqueous solution in the water-bath when the last traces of hydrarsine are expelled. Arsenious acid is removed by hydrated peroxide of iron, after which the kakodylic acid is again crystallized from alcohol. Ether, added to the mother-liquid, causes the deposition of more crystals.

Kakodylic acid forms brittle, glassy, transparent, colourless, regular four-sided prisms, with unequal acuminate planes, set obliquely on the lateral surfaces. It is inodorous, nearly tasteless, permanent in dry, deliquescent in moist air, soluble in water and alcohol, insoluble in ether. It has a feebly acid reaction, and forms with the alkalies gummy, amorphous compounds. It dissolves hydrated peroxide of iron and hydrated oxide of copper with the aid of heat. It is soluble in oil of vitriol, and crystallizes from it without change. It is not decomposed by anhydrous sulphuric acid, and is with difficulty oxidized by nitric acid or aqua regia.

It melts at 390° with partial decomposition, and congeals at about 195° to a radiated crystalline mass. At 445° it becomes brown, gives out vapours smelling of alkarsine, and deposits arsenic and arsenious acid.

When treated with protochloride of tin, phosphorous or phosphatic acid, it is converted into oxide of kakodyle by the loss of oxygen. In the watery solution, sulphuretted hydrogen does not cause a precipitate of sulphuret of arsenic. The liquid becomes milky, and when heated deposits oily drops of sulphuret of kakodyle. Kakodylic acid has no poisonous action on the animal body.

It ought to be mentioned here, that we may employ these compounds in testing for arsenic. If a metallic sublimate, supposed to be arsenic, be boiled with water containing air till it is dissolved, the solution mixed with potash and acetic acid, and evaporated to dryness, the residue, when heated in a test tube, gives off the horrible smell of oxide of kakodyle. If to the ignited mass a few drops of protochloride of tin be added, the still more penetrating odour of the chloride of kakodyle will be perceived. Antimony does not produce these effects. This test may also be employed to recognize the acetates. (Bunsen.)

Kakoplatyle.—This is another radical, discovered by Bunsen, the compounds of which are formed when bichloride of platinum, dissolved

in alcohol, is mixed with chloride of kakodyle also dissolved in alcohol. The radical is not yet known in the separate state. Its composition is $C_4H_6AsPtO = PtO, Kd$, that is, it contains the elements of kakodyle and protoxide of platinum.

In the experiment above mentioned, the chloride of kakoplatyle is obtained as a reddish-brown precipitate, which, when boiled with water, gives acicular crystals of the chloride. The bromide and iodide are also both crystalline, the former appearing in large yellow crystals, the latter in golden scales.

The oxide of kakoplatyle is basic and forms crystalline salts with acids. It would, appear, therefore, that kakoplatyle itself, like kakodyle, is analogous to metals. These compounds have not yet been fully studied.

CONSTITUTION OF ETHER AND ITS COMPOUNDS.

Ether and ammonia have a certain degree of analogy in their compounds, which was first pointed out by Dumas and Boullay; and as the view taken in France of the compounds of ammonia admitted the existence of ammonia and water, as such, in the ammoniacal salts, the analogy was extended to ether, which was considered the first hydrate of olefiant gas, alcohol being the second hydrate. In Germany and other countries a different view was taken of ammonia and its compounds. The water was supposed to form an integrant part of the base; its hydrogen, with the ammonia, forming ammonium, and its oxygen uniting with the ammonium to form an oxide. This view naturally led to the idea of organic oxides of compound radicals, possessing the characters of bases, as a kind of balance to the well-known organic acids, or oxides having acid characters. Hence ether was considered as an organic oxide of the radical ethyle, C_4H_5 ; and the existence of these conflicting opinions gave rise to a contest of ten years' duration, the immediate result of which was the discovery of a multitude of compounds, while science was enriched with numberless important observations. No department of organic chemistry has been so thoroughly investigated as that of the ethereal compounds; and now that the existence of organic oxides is universally admitted, the contest between the two theories of ether has ceased, while it cannot be said that the question has been decisively settled by experiment. Indeed, if, in the actual state of the science, we consider the compounds of ether and ammonia, it is easy to see that the opposite opinions were essentially the same, and that men disputed about them because they were not agreed on the interpretation of the phenomena; for these

two series of compounds assume the same form, if we consider amide as the radical of the ammoniacal series, and acetylene as that of the series of ether. They only differ in this, that the compounds of acetylene are frequently acid, which is not the case with those of amide.

Let Ad represent amide = NH_2 , and let Ac represent acetylene = C_4H_3 . We shall then have:—

COMPOUNDS OF ACETYLENE.

$\text{Ac} = \text{C}_4\text{H}_3 = \text{Acetylene}.$
 $\text{AcH} = \text{Olefiant Gas}.$
 $\text{AcH}_2 = \text{Ethylene}.$
 $\text{AcH}_2\text{O} = \text{Ether}.$
 $\text{AcH}_2\text{Cl} = \text{Chloride of Ethylene}.$
 $\text{AcH}_2\text{I} = \text{Iodide of Ethylene}.$
 $\text{AcH}_2\text{Br} = \text{Bromide of Ethylene}.$
 $\text{AcH}_2\text{O} + 1 \text{ at. Acid} = \text{Salts of Oxide of Ethylene}.$
 $\text{AcH}_2\text{O} + \text{HO} = \text{Alcohol}.$
 $\text{AcH}_2\text{S} + \text{HS} = \text{Mercaptan}.$
 $\text{AcH}_2\text{O} + \text{CS}_2 = \text{Xanthic Acid}.$
 $\text{AcPt} + \text{PtCl}_2 = \text{Acid in Zeise's Salt}.$
 $\text{AcPt}, \text{PtCl}_2 + \text{ClK} = \text{Zeise's Salt with Chloride of Potassium}.$
 $\text{AcPt}, \text{PtCl}_2 + \text{AdH}_2\text{Cl} = \text{Do. with Sal-ammoniac}.$
 $\text{AcH}_2 = \text{Olefiant Gas}.$
 $\text{AcH}_2 + 2\text{SO}_3 = \text{Isethionic Acid}.$
 $\text{AcO} = \text{Oxide of Acetylene}.$
 $\text{AcCl} = \text{Chloride of Acetylene}.$
 $\text{AcBr} = \text{Bromide of Acetylene}.$
 $\text{AcO} + \text{HO} = \text{Aldehyde}.$
 $\text{AcCl} + \text{HCl} = \text{Oil of Olefiant Gas}.$
 $\text{AcBr} + \text{HBr} = \text{corresponding compound with Bromine}.$
 $\text{AcCl} + \text{Pt}_2\text{Cl} = \text{Zeise's Acid}.$
 $\text{Ac} + \text{CO} \quad . \quad . \quad *$
 $\text{Ac} + \text{Bz} = \text{Oil of Cinnamon. (Dumas.)}$
 $\text{AcBz} + \text{NO}_3 + \text{aq.} = \text{Nitrate of Oil of Cinnamon}.$
 $\text{AcH}_2\text{O} + 2\text{C}_2\text{O}_3 = \text{Binooxalate of Oxide of Ethylene}.$
 $\text{AcO} + \text{O} = \text{Aldehydic Acid}.$
 $\text{AcO} + \text{O}_2 = \text{Acetic Acid}.$
 $\text{AcO} + \text{Cl}_2$
 $\text{AcO} + \text{Cl}$
 S
 $\text{AcO} + \text{S}_2$

COMPOUNDS OF AMIDE.

$\text{Ad} = \text{NH}_2 = \text{Amide}.$
 $\text{AdH} = \text{Ammonia}.$
 $\text{AdH}_2 = \text{Ammonium}.$
 $\text{AdH}_2\text{O} = \text{Oxide of Ammonium}.$
 $\text{AdH}_2\text{Cl} = \text{Sal-ammoniac}.$
 $\text{AdH}_2\text{I} = \text{Iodide of Ammonium}.$
 $\text{AdH}_2\text{Br} = \text{Bromide of Ammonium}.$
 $\text{AdH}_2\text{O} + 1 \text{ at. Acid} = \text{Salts of Oxide of Ammonium}.$
 $\text{AdH}_2\text{O} + \text{HO} = \text{compound in Sulphate of Ammonia}.$
 $\text{AdH}_2\text{S} + \text{HS} = \text{Hydrosulphuret of Ammonia (Hydrosulphuret of Sulphuret of Ammonium.)}$
 $\text{AdH}_2\text{S} + \text{CS}_2 = \text{Carbosulphuret of Sulphuret of Ammonium}.$
 $\text{AdHg} + \text{HgCl}_2 = \text{White Precipitate. (Kane.)}$
 $\text{AdPtCl} + \text{AdH}_2\text{O} = \text{new Base of Gros}.$
 $\text{AdPtCl} + \text{AdH}_2\text{Cl} = \text{compound of do. with Hydrochloric Acid}.$
 $\text{AdH} + \text{SO}_3 = \text{Rose's Anhydrous Sulphate of Ammonia}.$
 $\text{Ad} + \text{CO} = \text{Carbamide}.$
 $2\text{Ad} + 2\text{CO} + \text{Urea}.$
 $\text{Ad} + 2\text{CO} = \text{Oxamide}.$
 $\text{Ad} + \text{Bz} = \text{Benzamide}.$
 $\text{AdBz} + \text{C}_4\text{HO}_3 + \text{aq.} = \text{Hippuric Acid}.$

* $\text{Ac}, \text{CO} = \text{Oil of Cloves (Dumas)? Santonine? (C}_5\text{H}_3\text{O, Ettling). Ac}, 2\text{CO} = \text{Mannite} = \text{C}_6\text{H}_3\text{O}_2 + 4 \text{ aq. Caffeine, Asparagine, and many other substances, may also be introduced into the series of Acetylene, although with slender probability}.$

These formulæ require no explanation. They have been developed in order to show the extraordinary analogy between the series of ammonia and that of ether, and to explain how olefiant gas came to be considered by many as the first member of the series of ether. They show that the two opposed theories of ether have the same foundation, and render any farther dispute about the truth of either unnecessary. It is probable that, by searching for acetylene and amide in known substances, these series may be much extended.

Kane first proposed to consider the compounds of ether and ammonia according to the above view. Malaguti also constructed a similar table, considering ether as a compound of 2 at. hydrogen with 1 at. oxide of acetylene = AcO, H_2 .

In the following pages, the different kinds of sugar, and the products of their decomposition, are considered, as an appendix to the compounds of ethylene; chiefly, because from them are derived alcohol, and consequently all the compounds of ethylene; and also, because the uncertainty in which we are as to their true constitution renders it impossible to arrange them on scientific principles.

SUGAR.

If we understand by sugar all those substances which are susceptible of the vinous fermentation, that is, which by a peculiar decomposition are resolved into alcohol and carbonic acid, we shall include under this head the following substances: cane sugar, grape sugar (sugar of starch, of honey, of diabetes), uncrystallizable sugar of milk or lactine, and mushroom sugar, found by Wiggers in the ergot of rye.

CANE SUGAR.

Formula, $\text{C}_{12}\text{H}_{20}\text{O}_{11} + 2\text{HO}$. Occurs in the juice of the sugar-cane, of the maple, of beet-root (and many similar roots, as carrots, turnips, &c.), of *Juglans alba*, in potatoes, in the root of *Althæa officinalis*, in the nectaries of most flowers, in the tubers of *Lathyrus tuberosus*, &c.

Pure sugar is prepared from these juices by crystallization, after they have been clarified by means of milk of lime, blood, milk, &c. When made to cool rapidly, it forms small cohering crystals, which constitute loaf-sugar, or white sugar. When slowly crystallized, it forms regular large transparent crystals, known as sugar-candy.

Sugar is colourless, but, when impure, yellow or brown; and forms hard, transparent, easily cleavable, four-sided and irregular six-sided

prisms, acuminated on two surfaces; sp. gr. 1.6065; friable, phosphorescent when rubbed in the dark, permanent in dry air. At 365° (285°, Proust), according to Peligot, it melts into a viscid colourless liquid, which by sudden cooling forms an amorphous transparent mass (barley-sugar). This, when kept, becomes opaque and brittle, and then shows the usual planes of cleavage of sugar. At 400° to 420° sugar is converted into caramel, losing 3 at. water. At a higher temperature, it yields combustible gases mixed with carbonic acid, empyreumatic oil, acetic acid, and a residue of one-fourth of its weight of carbon. (Cruikshank.)

Cane sugar dissolves in one-third of its weight of cold water, in hot water to any extent. A solution, saturated at 230°, forms on cooling a mass composed of small cohering crystals. A solution saturated in the cold has a viscid consistence, and is called syrup. If kept long at a temperature near the boiling point, the syrup loses the power of crystallizing. When syrup is boiled, the bubbles of vapour burst with an audible noise, owing to the viscosity of the liquid. One-twentieth part of oxalic, citric, or malic acids, instantly renders the boiling syrup thin, and deprives the sugar of the power of crystallization, which cannot now be restored by means of alkalies, although the sugar is still capable of undergoing fermentation. Here, the sugar is converted into a different allotropic condition, which is amorphous. When heated with dilute sulphuric acid (Kirchhof, Pelouze), or with tartaric acid (Guibonrt), it is converted into grape sugar.

Oil of vitriol dissolves sugar with a brown colour. If the superfluous acid be removed by chalk, there remains a compound of sugar with sulphuric acid, which blackens on evaporation, with disengagement of sulphurous acid. (Braconnot.) This compound is *saccharo-sulphuric acid*, which is accompanied by a brown substance, also possessed of acid properties. When loaf-sugar is moistened with oil of vitriol, a violent reaction takes place after some time, sulphurous and formic acids being disengaged. The sugar forms a soft coal-black paste, which, when washed with water, leaves a black carbonaceous powder. Sugar, when kept for a long time at a high temperature dissolved in dilute sulphuric acid, absorbs oxygen from the air, formic acid is produced, and a brown insoluble matter is deposited, which Malaguti considers identical with the matter formed by the decay of wood, to which the name of *humus* or *humic acid* has been given.

Hydrochloric acid readily dissolves sugar, and forms a black, thick, resinous paste. Nitric acid changes it into saccharic, oxalic, and carbonic acids: 100 parts of sugar yield 54 (Cruikshank), or upwards of 67 (Thenand), of oxalic acid.

When arsenic acid is added to syrup, the mixture after some hours becomes pink, then purple, and, lastly, brown, and the odour of acetic acid is perceived. Acids and alkalies do not change this colour. If all the arsenic be precipitated by sulphuretted hydrogen, there remains a pale yellow sweet liquid, not precipitated by acetate of lead. (Elsner.)

Cane sugar dissolves carbonate of copper and verdigris, forming green solutions, from which the oxide is not precipitated by alkalies. The salts of oxide of copper and peroxide of iron, when mixed with sugar, are no longer precipitable by alkalies. Hydrated oxide of copper dissolves, with the aid of alkalies, in a solution of sugar, with a violet colour. When all these solutions are heated, metallic copper or suboxide of copper is precipitated, the latter sometimes pure, and sometimes mixed with a brown substance soluble in ammonia, and the liquid contains formic acid. (Wöhler.) A solution of cane sugar, heated with nitrate of silver, causes a black precipitate.

Bichloride of mercury is reduced to calomel, and chloride of copper to subchloride, by the action of sugar; and chloride of gold in the same circumstances yields a red precipitate.

Chlorine gas, passed through a boiling solution of sugar, decomposes it. Hydrochloric acid is formed, along with another uncrystallizable acid (Simonin), malic acid? (Chenevix). According to Liebig, this decomposition is very incomplete. Sugar in powder slowly absorbs moist chlorine, and is changed into a brown deliquescent mass, containing hydrochloric acid, while carbonic acid is disengaged. (Priestley, Bouillon Lagrange, Vogel.) Dry chlorine, passed over dry sugar, does not act on it. (Liebig.)

Sugar is much employed, from its antiseptic power, to preserve vegetable and animal matters. In pharmacy it is used for syrups, electuaries, conserves, &c. Sugar, taken along with other food, is a nourishing article of diet; but if taken alone, or at least without any nitrogenised substance, it cannot long support life. (Magendie.)

Biot has observed, that a ray of polarized light, when passed through a solution of cane sugar, exhibits in the plane of polarization a succession of the prismatic colours, when that plane is turned round to the right hand.

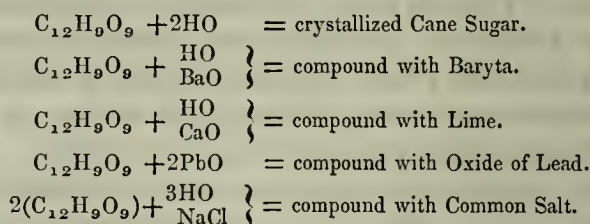
Cane sugar forms with the alkalies, with oxide of lead, and with common salt, what appear to be saline combinations.

It is sparingly soluble in cold alcohol, and requires 80 parts of boiling alcohol for solution; but 4 parts of spirit of wine, sp. gr. 0.880, dissolve 1 of sugar.

COMBINATION OF SUGAR WITH BASES.

The property possessed by sugar, of combining with certain bases,—of dissolving, for example, a much larger quantity of lime than pure water,—has long been known. Berzelius and Peligot have analysed the compound of sugar with oxide of lead, and Peligot those with baryta and lime.

In these compounds crystallized sugar loses 1 eq. water, which is replaced by 1 eq. of metallic oxide or chloride of sodium. The following are the formulæ of these compounds :—



The first two compounds dissolve several metallic oxides, when an excess of sugar is added. Probably double compounds are formed, but these have not been obtained in crystals. The solutions of these two compounds have a strong alkaline reaction, and absorb carbonic acid readily from the air, while a certain quantity of sugar is set free, giving a sweet taste to the compound. In the dry state they may be preserved without change. When kept dissolved, an excess of alkali appears to facilitate their decomposition. Braconnot observed, that a solution of the compound with lime, kept for four years in a bottle imperfectly stopped, deposited a precipitate composed of carbonate, oxalate, and another salt of lime, the acid of which was uncrystallizable, very sour, and gave with salts of lead, or with lime-water, a precipitate soluble in an excess of the acid. The liquid still contained uncrystallizable sugar, and a peculiar substance combined with lime, which was precipitated by alcohol as a viscid mass. Sulphuric acid, added to the same liquid, formed a precipitate of sulphate of lime, disengaging acetic acid.

A solution of cane sugar, boiled with excess of caustic potash, is gradually changed into grape sugar, which itself is converted by the alkali into potassio-saccharic acid. (Peligot.)

Powdered sugar absorbs ammoniacal gas, and is changed into a flexible mass, compact and crystalline at the surface, and smelling strongly of ammonia. (Berzelius)

Indigo in contact with solution of sugar and potash, or soda in ex-

cess, easily yields oxygen to the sugar, and is converted into deoxidized or white indigo. The sugar is changed into formic acid. (Wöhler.)

Compound of Sugar with Lime.—Formula, $C_{12}H_9O_9 + \begin{Bmatrix} CaO \\ HO \end{Bmatrix}$.

(Peligot.) By exposing to a moderate heat a solution of sugar along with hydrate of lime, there is obtained a bitter alkaline liquid, containing, for 100 parts of sugar according to Daniell, 50 parts, according to Osann, 56 parts of lime. This solution, when boiled, becomes turbid, and forms a gelatinous mass, like the jelly of starch, but becomes again liquid by cooling. (Löwitz; Osann.) The precipitate is a compound of sugar and lime, atom to atom, containing 14 p. c. of lime. It is purified by washing with boiling water, in which it is insoluble; or it may be obtained by adding alcohol to the solution of lime with excess of sugar.

The solution of this compound exposed to the air deposits regular acute rhomboids of hydrated carbonate of lime. (Pelouze.)

Compound of Sugar with Baryta.—Formula, $C_{12}H_9O_9 + \begin{Bmatrix} HO \\ BaO \end{Bmatrix}$.

By mixing a solution of 1 part of baryta in 3 of water with a solution of 2 parts of sugar in 4 of water, there is obtained after some time a crystalline semi-solid mass, which is increased by a gentle heat. It is washed with cold water, care being taken to avoid the contact of carbonic acid: the dry compound forms small brilliant crystals in foliated scales like boracic acid.

The solution of these crystals has an alkaline taste and reaction. Carbonic acid and other acids restore the sweet taste by neutralizing the base, and setting free the sugar.

Peligot, who analysed this compound, found 28.1 p. c. of carbon, 4.14 of hydrogen, and 31 of baryta; and, not having reckoned that portion of the carbon ($\frac{1}{12}$ th) retained by the baryta, he adopted the formula $C_{12}H_9O_9 + \begin{Bmatrix} 2HO \\ BaO \end{Bmatrix}$. When this correction is made, however, his analysis corresponds exactly to the formula $C_{12}H_9O_9 + \begin{Bmatrix} HO \\ BaO \end{Bmatrix}$, which is also much more probable. According to the first, sugar combines with baryta without losing water; according to the latter, one equivalent of water is replaced by one equivalent of baryta.

Compound of Sugar with Oxide of Lead.—Formula, $C_{12}H_9O_9 + 2PbO$. (Peligot.) A boiling solution of sugar dissolves oxide of lead, and deposits a white precipitate, which is obtained quite pure by washing with boiling water. The mother-liquid contains a soluble compound of sugar with oxide of lead.

A mixture of a concentrated solution of sugar with one of acetate of lead deposits a gelatinous precipitate, which is to be washed with cold water, and afterwards dissolved in boiling water. This solution, left to itself in a closed bottle, deposits the salt gradually in the form of white mamillary groups of crystals. These are washed with cold water, and dried in vacuo, or in a box beside quicklime. Berzelius, who also analysed this compound, obtained 58.26 p. c. of oxide of lead, and adopted the formula $C_{12}H_{10}O_{10} + 2PbO$. But Peligot, on repeating his analysis, succeeded in proving satisfactorily that the salt contains 59 p. c. oxide of lead, and the other elements in proportions exactly corresponding to the formula $C_{12}H_9O_9 + 2PbO$.

Compound of Sugar with Chloride of Sodium.—Formula, $2(C_{12}H_9O_9) + \left\{ \begin{smallmatrix} 3HO \\ NaCl \end{smallmatrix} \right\}$. (Peligot.) This compound is obtained by the spontaneous evaporation of a solution of 1 part of common salt, and 4 parts of sugar. Candy sugar is first deposited, and the solution, decanted off these crystals, at last deposits the new compound. It has a taste both sweet and saline, and deliquesces in a moist air.

GRAPE SUGAR.

Syn. Glucose (Dumas); Diabetic Sugar; Sugar of Starch; Sugar of Fruits.—Formula, $C_{12}H_{14}O_{14}$. The sweet taste of grapes, of most acid fruits, of honey, &c. proceeds from this kind of sugar. It is also a product of the decomposition or transformation of a variety of substances. Thus, cane sugar, starch (Löwitz), woody fibre (Braconnot), sugar of milk (Vogel), when boiled with dilute acids, furnish grape sugar. Starch yields it, according to De Saussure, by spontaneous decomposition; according to Kirchhof, by the action of the gluten of malt. It is found ready formed in the urine of persons affected with diabetes mellitus.

To obtain the sugar contained in ripe grapes, the juice is neutralized with chalk, clarified by white of egg, and evaporated till it crystallizes. From dry raisins it is obtained by pounding them, and acting on the mass with cold alcohol to remove the uncrystallizable sugar, pressing the whole, redissolving in water, neutralizing with chalk, clarifying as before, and evaporating. Fresh honey appears to contain grape sugar in a particular state. In the comb it forms a clear syrup, very viscid, and retains this character if kept in a dry place; but when separated from the wax, by melting in water, a diluted liquor is obtained, which after some days forms a crystalline mass, having more consistence than the honey, although containing one-fourth of

its volume of water in addition. The solid parts of this mass are grape sugar.

It may be extracted from diabetic urine by evaporating that liquid till it crystallizes. The crystals are washed on a filter with cold alcohol, and the white residue is redissolved in water and purified by recrystallization.

To convert sugar of milk into grape sugar, 100 parts are dissolved in 400 of water, 2 parts of sulphuric acid are added to the mixture, and the whole is exposed to a temperature near the boiling point for three or four hours. The liquid is then neutralized with lime or baryta, to separate the sulphuric acid, and evaporated to a syrup, when the grape sugar crystallizes after three or four days.

Preparation of Grape Sugar from Starch.—1. By sulphuric acid. One part of potato starch, 4 parts of water, and from $\frac{1}{100}$ th to $\frac{1}{10}$ th of sulphuric acid are boiled for thirty-six to forty hours, renewing from time to time the water as it evaporates. Under a high pressure, or at a higher temperature, the change may be effected in a shorter time and with a smaller proportion of sulphuric acid. When a thin paste of starch and water is slowly poured into the boiling diluted acid, it speedily loses the consistence of jelly which it at first acquires; and, when the operation is performed on the large scale, the contact alone with the dilute acid for ten or twelve hours is sufficient to change the starch into grape sugar, provided the mixture is not allowed to cool too rapidly.—2. By means of malt. The paste of starch speedily loses its gelatinous consistence if an infusion of malt be poured on it. It then forms a mobile liquid, and if there be enough of malt, the starch is completely changed into grape sugar at the end of some hours, provided the mixture be kept at the temperature of 160° to 170° . Six parts of malt produce on an average 25 parts of grape sugar. As soon as the liquid ceases to strike a blue colour with iodine, or to be precipitated by acetate of lead or alcohol, we may be certain that all the starch is changed into grape sugar.

Preparation of Grape Sugar from Woody Fibre.—Twelve parts of linen or paper cut in small pieces are intimately mixed by degrees with 17 parts of strong sulphuric acid (Braconnot); or, what is better, with 5 parts of sulphuric acid and 1 of water (Vogel). All rise of temperature must be carefully avoided. After twenty-four hours the pitchy mass is dissolved in a large quantity of water, and boiled for ten hours. The liquid is then neutralized with chalk, filtered, and, after evaporating to the consistence of syrup, the residue is set aside to crystallize.

According to Brunner, 100 parts of starch produce 104 to 106 of grape sugar. According to De Saussure 110, and according to Bra-

cannot 100, parts of linen rags yield 114 of sugar, and even 115·7, according to Guérin. By calculation 100 parts of starch, by combining with 4 atoms of water for one of starch, should yield 122·03 parts of crystallized grape sugar.

If we compare the composition of starch, sugar of milk, woody fibre, and cane sugar with that of grape sugar, we perceive that they all contain the same quantity of carbon, united with different quantities of oxygen and hydrogen in the proportions to form water; and that grape sugar contains the most oxygen and hydrogen. We obtain exactly the composition of crystallized grape sugar by adding 6 atoms of water to the elements of 1 atom lignine (woody fibre), 4 atoms to starch, 3 atoms to cane sugar, and 2 atoms to crystallized sugar of milk.

In what manner does malt act in converting starch into sugar? This question is yet to be answered. As to the action of sulphuric acid on starch, it appears to be quite analogous to the formation of ether by the decomposition of bisulphate of oxide of ethyle. At least, starch and sulphuric acid form a crystalline compound, according to De Saussure, and a gummy compound described by Guérin; these compounds are neutral, and are resolved by boiling into grape sugar and free sulphuric acid.

Before becoming grape sugar, starch is converted into a substance resembling gum, which gives a wine-red colour with iodine. Payen and Persoz have called it *Dextrine*, because it has the property of causing the plane of polarization to deviate to the right hand. Frémy has observed that in the conversion of starch into grape sugar, there is obtained a variable quantity of *mannite*.

It appears that the quantity of grape sugar in diabetic urine has a direct proportion to the quantity of fecula in the food of the patient, such as bread, potatoes, &c. But as the experiments of Gerhardt have rendered it probable that animal gelatine, acted on by sulphuric acid, yields fermentescible sugar, we may naturally suspect that the proximate principles of the body are also concerned in the production of sugar in diabetes.

Grape sugar crystallizes from an alcoholic solution in square tables or hard transparent cubes. (De Saussure.) A concentrated aqueous solution forms on standing a spongy mass, composed of minute crystalline grains. It often happens, in crystallizing grape sugar on a large scale from a moderately strong syrup, that there are deposited hard hemispherical masses composed of needles radiating from a centre. The sp. gr. of grape sugar is 1·386. (Guérin.)

Grape sugar is less soluble, and dissolves more slowly in water than cane sugar; it is much sweeter when dissolved than in the solid form:

2½ parts of grape sugar are required to produce in a liquid the same intensity of sweetness as is caused by 1 part of cane sugar.

At 212° grape sugar melts, losing 9 p. c. = 2 at. water. When heated beyond 285°, it passes into caramel. The sugar produced from starch by malt becomes soft at 140°, pasty at 158°, and syrupy between 194° and 212°, losing 98 p. c. of water. (Guérin.) It is soluble in 1½ parts of cold water, and to any extent in boiling water. The syrup which it forms is less viscid than that of cane sugar.

It is very soluble in cold alcohol; at 77° it dissolves in 8 parts of alcohol of 85 p. c., and in 20 parts of absolute alcohol. Almost the whole of the sugar dissolved by boiling alcohol is deposited, on cooling, in crystalline grains, which contain alcohol in combination.

It has been already mentioned that a ray of polarized light, passed through a solution of cane sugar, produces in the plane of polarization a suite of coloured rings when the plane of polarization is made to rotate from left to right. Uncrystallizable cane sugar, and the sugar in the juice of the grape, produce the same phenomenon by a rotation from right to left; as do also, although with less brilliancy of colours, crystallized grape sugar, sugar of starch, and diabetic sugar. This characteristic property is in no way affected by the commencement of fermentation in these latter kinds of sugar, but the case is different with cane sugar. As soon as it is made to ferment, the coloured rings are no longer visible by rotation from left to right, but appear as soon as the plane of polarization is made to rotate from right to left; because, apparently, before being resolved into alcohol and carbonic acid, it assumes the form of grape sugar. (Biot.)

The reactions of grape sugar with acids and alkalies essentially distinguish it from cane sugar. Thus, oil of vitriol chars cane sugar, and diluted sulphuric acid converts it into an insoluble brown matter; while oil of vitriol dissolves grape sugar, producing only a slight yellow or brown colour, and forms with it a new acid, not precipitable by baryta—(sulpho-saccharic acid). On the other hand, alkalies, which do not alter the colour of cane sugar, even by boiling, provided the solutions be dilute, convert grape sugar into a brown or black substance with the aid of heat.

Peroxide of lead forms with grape sugar, at 212°, bibasic formiate of lead, water, and carbonate of lead. (A. Sturenburg.)

The compounds of grape sugar with lime, baryta, and oxide of lead, are prepared with difficulty; while it forms with ease a crystallized compound with common salt.

Although the identity of the different kinds of sugar classed under the name of grape sugar or *glucose* be generally admitted, it is import-

ant to know that there are certain facts apparently irreconcilable with this notion. For example, diabetic sugar, dried in vacuo, is represented, according to Peligot and Prout, by $C_{12}H_{14}O_{14}$; while sugar of starch prepared by malt, according to Guérin, loses in vacuo 2 at. water, and becomes $C_{12}H_{12}O_{12}$.

All experimenters on this subject agree that the sugar made from starch by sulphuric acid, the sugar of honey, and that made with malt, melt before 212° , and lose water. All these facts would go to show that the formula $C_{12}H_{14}O_{14}$ does not correspond to its composition at this temperature; but De Saussure, on the other hand, obtained in the analysis of grape sugar, crystallized, and dried at 212° , results closely agreeing with that formula.

GRAPE SUGAR WITH BASES.

Peligot and some other chemists consider cane sugar and grape sugar as bodies which act towards bases like acids, producing with them regular salts, which they call Saccharates. To this view Graham objects, that no acid is known which does not combine with potash and soda; which none of the sugars do. He considers sugar as a hydrated body, analogous rather to a hydrated salt, in which a certain portion of water is contained in a form different from water of crystallization, and may be replaced by oxide of lead, lime, or baryta, producing basic salts. Potash, soda, and oxide of silver, on the contrary, never replace but the truly basic water in a compound; for which reason these bases form no subsalts (basic salts). This explains why they do not combine with sugar. Although these views of Graham are not absolutely established, since bodies exist, such as allantoine and others, capable of uniting with oxide of silver, although we cannot make them unite with potash, soda, or baryta, yet when we reflect that sugar easily combines with common salt, forming a compound exactly like a double salt, we must admit that they acquire a high degree of probability.

If the compounds of sugar with bases are to be considered as salts, and sugar as an acid, we must also consider pyroxilic spirit as an acid; for it combines with lime and baryta, exactly like sugar, and also unites with chloride of calcium.

Grape Sugar and Common Salt.—This compound crystallizes in fine double six-sided pyramids; and is the only compound of grape sugar the composition of which is known with certainty.

It is obtained by saturating with sea-salt a moderately strong solution of grape sugar, and evaporating gently. Chloride of sodium is first deposited, and afterwards the bottom of the vessel is covered with

crystals of the compound, easily recognized by their form and their hardness. They are purified by repeated crystallizations. They are colourless, transparent, friable, soluble in water, very sparingly soluble in alcohol of 96 p. c.

According to the recent analyses of Erdman and Lehmann, these crystals contain water, and lose 2 at. = 4.337 p. c. at 212°. According to Peligot, they lose at 320° 3 at. water = 6.1 p. c. The crystals are $2(C_{12}H_{12}O_{12}) + NaCl + 2HO$.

The compound dried at 212°, according to Erdmann and Lehmann, is $2(C_{12}H_{12}O_{12}) + NaCl$. According to Peligot, when dried at 320°, the compound is $C_{24}H_{23}O_{23} + NaCl$. But Erdmann states that, after exposure to that temperature, it no longer contains sugar, but a modified matter. This, at all events, is the case when the compound is formed from diabetic sugar, sugar of starch, or sugar of dried raisins.

Grape Sugar and Oxide of Lead.—To prepare it, a solution of acetate of lead, to which ammonia has been added, is mixed with an excess of solution of sugar. The precipitate ought to be washed and dried in vacuo at the ordinary temperature. When dried in vacuo at 300°, it becomes yellow. With the aid of heat a solution of grape sugar dissolves a large quantity of oxide of lead; but the insoluble basic compound is difficult of preparation in this way, as the mixture cannot be boiled without becoming brown. One hundred parts of crystallized grape sugar, in combining with oxide of lead, lose 11.14 p. c. of water; the residue is brown, and has the smell of caramel, even when the temperature has not exceeded 140°. (Berzelius.) This loss corresponds to 5 at. water for 2 at. crystallized sugar. Hence, the substance combined with oxide of lead must be $C_{24}H_{23}O_{23}$; which is the same as that found by Peligot in the compound with common salt, when dried at 320°.

The insoluble compound obtained from grape sugar and the ammoniacal acetate of lead has been analysed by Peligot, who states its formula to be $C_{24}H_{21}O_{21} + 6PbO$. This would imply that the crystallized sugar lost 7 at. water, which were replaced by 6 at. oxide of lead. But on re-calculating Peligot's analysis, his results will be found to agree more closely with the formula $C_{12}H_{11}O_{11} + 3PbO$, according to which 3 at. water are replaced by 3 at. oxide of lead. As this is in accordance with all our experience of such substitutions, we must reject Peligot's formula. It will then appear that the grape sugar in this compound with oxide of lead has the composition of crystallized cane sugar.

Grape Sugar with Lime and Baryta.—These bases are freely dissolved by solution of grape sugar, diminishing its sweetness. The

solutions are alkaline, and become brown when heated. When lime enough is added to destroy the sweet taste, there is obtained by cautious evaporation a viscid mass soluble in alcohol. An excess of lime produces a basic compound, which alcohol precipitates in a coagulum. This precipitate, washed with alcohol, forms a white mass, which becomes semi-transparent by attracting moisture from the air. When dried, and it is difficult to dry it without turning it brown, it contains 24.26 p. c. of lime; which indicates that 2 at. lime have replaced 2 at. water in the sugar. When decomposed by carbonic acid, it yields unaltered sugar.

Peligot obtains a compound of grape sugar with baryta, by dissolving them separately in pyroxylic spirit, and mixing the solutions, that of the sugar being in excess. A flocculent precipitate is formed, which, when washed with pyroxylic spirit, pressed in bibulous paper, and dried in vacuo beside oil of vitriol and quicklime, appears as a light porous powder. The presence of water causes it to turn brown in drying. When dried at 212° it becomes yellow, and contains 35.37 p. c. of baryta; and its formula, according to Peligot, is $(2C_{12}H_{14}O_{14}) + 3BaO$. But this is very improbable, as it would imply that 2 atoms of crystallized sugar combine with 3 atoms of baryta, without losing water, even at 212° ; whereas the sugar alone loses 2 atoms of water at 212° . It appears, moreover, that Peligot omitted to reckon the amount of carbonic acid which must have remained in the combustion tube in combination with the baryta.

SULPHO-SACCHARIC ACID.

Discovered by Peligot.—To prepare it, 1 part of sugar of starch is melted in the water-bath, and mixed with $1\frac{1}{2}$ parts of oil of vitriol, taking care to add the acid gradually, to agitate well, and to keep the mixture cold, if necessary, by plunging the vessel into cold water. If this be neglected, or if the sugar be impure, the product is coloured. The whole is dissolved in water, and saturated with carbonate of baryta, which precipitates the free sulphuric acid, while the sulpho-saccharate of baryta remains in solution. When this solution is treated with subacetate of lead, the precipitate first formed is coloured, and is separated; that which falls afterwards is white. Peligot analysed it after drying it at 212° . Of two analyses, one led to the formula $2(C_{12}H_{10}O_{10}),SO_3 + 4PbO$; the other to the formula $2(C_{12}H_{12}O_{12}),SO_3 + 4PbO$. As the object of the author was merely to prove the existence of the acid, we are at present ignorant of its true

composition. From the salt just mentioned the acid may be obtained by means of sulphuretted hydrogen.

The sulpho-saccharic acid forms a sweet liquid, slightly acid, reddening vegetable blues, but not precipitating the salts of baryta, and forming soluble salts with almost all bases. It is decomposed by evaporation at a gentle heat, or even at the ordinary temperature in vacuo, being resolved into sugar and sulphuric acid, which now precipitates the salts of baryta.

PRODUCTS OF THE DECOMPOSITION OF CANE SUGAR AND GRAPE SUGAR.

By the prolonged action of a high temperature and a small quantity of diluted sulphuric acid, cane sugar passes into the state of grape sugar which has the property of combining with sulphuric acid. There is every reason to believe that the modification which small quantities of organic acids produce in cane sugar at the boiling temperature is of the same nature; that is, that grape sugar is produced, which instantly unites with the acid that has been added. These new combinations have a sweet taste, and may be made to enter into fermentation by means of a small quantity of ferment; but they are uncrystallizable, and, when much concentrated by heat, solidify into an amorphous mass, which absorbs moisture from the air, and is again converted into syrup. Tartaric, oxalic, citric, malic, kinic, and even acetic acids, form such compounds, and thus impede the crystallization of sugar; alkalies can no longer remove the acid, nor restore to the sugar the power of crystallizing. This is the reason why we cannot obtain crystallizable sugar by evaporating the sweet juices of plants which have an acid reaction. The syrup which they yield has every property of sugar, except that of crystallizing. It was formerly considered a separate species of sugar, and described as sugar of molasses; but it is now known with certainty to be common sugar, combined with acids.

The molasses, or treacle formed in the refining of cane sugar, contains the products of the decomposition of sugar by alkalies.

ACTION OF ACIDS ON SUGAR.

A cold solution of cane sugar, with a little dilute sulphuric acid, is by degrees entirely converted into grape sugar; while the same acid, if concentrated, rapidly chars it. Now we have seen that grape sugar

may be triturated with strong sulphuric acid without blackening; it is therefore obvious that the change produced by the acid when it chars cane sugar must take place before it has been converted into grape sugar.

Strong hydrochloric acid acts like sulphuric acid; when diluted and boiled with the sugar, it converts it into a solid, brown, gelatinous mass, soluble in water with a brown colour, which is purified by repeated washing with water.

The aspect and external properties of this substance do not vary, whatever be the strength of the acid or the heat employed; but its composition is totally changed. Thus, when sugar is boiled with 1 part of hydrochloric acid, diluted with 1 part of water, the product when dry is a brown or brownish-black powder, extremely light; its formula, when dried at 284° , is $C_{24}H_{11}O_9$. (Stein.) Along with this substance are produced formic acid and grape sugar. With a weaker acid, and at a lower temperature, there are formed two reddish-brown substances; one soluble in alkalies, the other insoluble. The formula of the insoluble compound is $C_{40}H_{16}O_{14}$; that of the other is $C_{40}H_{14}O_{12}$. By the influence of a prolonged boiling with a stronger acid, there are formed two black substances: one soluble in alkalies, the formula of which is $C_{40}H_{12}O_{12}$; the other insoluble, the formula of which is $C_{40}H_{16}O_{12}$. (Mulder.)

By boiling sugar with dilute sulphuric acid, Malaguti and Boullay obtained two substances which they considered identical with ulmine and ulmic acid, and to which therefore they gave these names; but there is every reason to believe that these substances only resemble the products of the decomposition of woody fibre in their colour, and that their chemical properties are different. One of these bodies is soluble in ammonia and the fixed alkalies, the other insoluble. We shall call the former *sacchulmic acid*, and the latter *sacchulmine*.

Sacchulmine is obtained by boiling for a very long time cane sugar in very diluted sulphuric, hydrochloric, or nitric acids. For 10 parts of sugar, 30 of water and 1 of sulphuric acid may be taken. The sacchulmine is deposited in brown scales, crystalline and brilliant, which are always contaminated with sacchulmic acid. The latter is easily removed by ammonia, in which it is soluble.

Sacchulmic Acid.—Formula, $C_{30}H_{15}O_{15}$. (Malaguti.) This acid dissolves in ammonia and the fixed alkalies, giving them a brown colour. It is precipitated from the solutions by acids as a brown flocculent powder. The alkaline earths and metallic salts also cause brown precipitates in these solutions.

When dry, it is a light brown powder, insoluble in alcohol and

ether. By long boiling in water it is converted into sacchulmine, thus losing its solubility in alkalies, without any change of composition.

According to Malaguti and Boullay, the analysis of this acid leads to the formula C_2HO ; but the salt which it forms with oxide of copper contains from 10 to 11 p. c. oxide of copper, which leads to the atomic weight of 4061 for the acid, and consequently to the formula $C_{30}H_{15}O_{15}$, a multiple of the above. It would appear to combine with oxides without losing water; but it is still uncertain whether the acid in the salts has the same composition as the free acid.

When sugar is boiled with dilute sulphuric acid for several days in open vessels, there is produced, besides these substances, formic acid, by means of the oxygen of the atmosphere. From 20 parts of cane sugar, 60 of water, and 1 of sulphuric acid, boiled for eighty-four hours, Malaguti obtained 6.5 parts of sacchulmine and sacchulmic acid, and 2.236 parts of dry formic acid. The formic acid is not produced when air is excluded.

PRODUCTS OF THE ACTION OF ALKALIES ON SUGAR.

Cane sugar is not coloured by being boiled with aqua potassæ, or with lime or barytic water; but if the heat be prolonged, and air admitted, the liquid becomes brown, and formic acid is produced, which combines with the alkali. The liquid contains, besides, two new acids, of which one is brown, and insoluble in water; the other is colourless, and attracts water from the air. Dumas has called these acids, which were first discovered by Peligot, *Melassic Acid* and *Glucic Acid*. In this operation the cane sugar is probably first converted into grape sugar, which is rapidly changed by alkalies into these acids.

Glucic Acid.—To prepare this acid, a solution of grape sugar is saturated with baryta or lime, and left to itself. After some weeks the liquid has no longer an alkaline reaction, and the base it contains can no longer be precipitated by a current of carbonic acid. By adding subacetate of lead, a bulky white precipitate is formed, which, when decomposed by sulphuretted hydrogen, yields an aqueous solution of the acid.

This acid is very soluble in water; when dried in vacuo, it forms an uncrystallized mass like tannin. It attracts rapidly the moisture of the air. Its solution has a decidedly sour taste, and reddens litmus. All its neutral salts are soluble. The basic salt of lead alone is insoluble. Peligot, who analysed this salt, gives for it the formula

$C_{24}H_{15}O_{15} + 6PbO$. But, as the analyses have not yet been sufficiently multiplied to fix its composition, we may observe that the formula $C_{12}H_8O_8 + 3PbO$ corresponds still better to the results of his analysis. Either formula will explain the formation of the acid; for as grape sugar, in the compound it forms with lead, has the formula $C_{12}H_{11}O_{11}$, to form glucic acid it has lost 3 at. water, which are replaced by 3 at. oxide of lead. Or if we consider anhydrous glucic acid to be $C_{24}H_{15}O_{15}$, and anhydrous grape sugar to be $C_{24}H_{21}O_{21}$, they will differ by 6 at. water.

Melassic Acid.—This acid is produced by the combined action of alkalis and heat on grape sugar. When a hot saturated solution of baryta or a solution of caustic potash or soda is mixed with melted grape sugar, the latter is dissolved with heat and disengagement of the vapour of water. The mixture acquires a brown colour, which becomes more and more intense if the heat be continued. Glucic acid is first formed, by the decomposition of which melassic acid is produced. The dark-brown solution is treated with excess of hydrochloric acid, which precipitates the melassic acid as a black flocculent powder. It is washed, first with diluted muriatic acid, afterwards with water.

Peligot analysed it, and from his results Dumas has deduced the formula $C_{24}H_{12}O_{10}$.

Besides melassic acid, there is found in combination with the alkali a substance which is not volatile, and which reduces the salts of silver with great facility. Qu. Is not this saccharic acid?

ACTION OF HEAT ON SUGAR.

Caramel.—Cane sugar melts at 365° into a viscid colourless liquid, which on cooling forms a transparent amorphous mass (barley-sugar). At a temperature somewhat higher it becomes brown; at from 400° to 430° it swells up, and is converted into a black porous mass, having a high lustre, like anthracite, called by Peligot *Caramel*. In this operation water alone is expelled, with a minute trace of empyreumatic oil and acetic acid.

The caramel of commerce contains a variable proportion of sugar. It is purified from sugar, and from certain bitter compounds which are always present in burnt sugar, by dissolving it in water and adding alcohol, which precipitates the caramel in a state of purity, retaining in solution the foreign matters.

Pure caramel is a black or brownish-black powder. It dissolves readily in water, giving it a fine sepia tint. Its solution has no taste,

and no action on vegetable colours. It is not susceptible of fermentation, and is insoluble in alcohol.

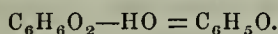
The solution of caramel precipitates the salts of baryta and the basic salts of lead. The composition of the barytic precipitate is variable; it contains from 20 to 21 p. c. of baryta.

When sugar is still more strongly heated, the caramel loses an additional quantity of water, and forms an insoluble compound. At a still higher temperature inflammable gases are given off, and a bulky coal is left, difficult of combustion.

According to Peligot, caramel has the same composition as cane sugar in its compound with oxide of lead, that is, $C_{12}H_9O_9$. Crystallized cane sugar, therefore, to form caramel, loses 2 at. of water. Grape sugar produces the same substance when similarly treated.

Metacetone.—Formula, C_6H_5O . (Fremy.) This substance is obtained by distilling an intimate mixture of 1 part of sugar and 3 parts of finely powdered quicklime. When the temperature reaches 285° , it suddenly rises of itself, and there is disengaged a small quantity of an inflammable gas, with an inflammable liquid, which is a mixture of acetone and metacetone. The addition of water separates the metacetone, which is purified by rectification, the last portions which distil being preserved.

It is a colourless liquid, having a pleasant odour. It boils about 183° , is miscible with alcohol and ether, but not with water. It may be regarded as acetone minus 1 at. water.



One atom of anhydrous sugar contains the elements of

$\frac{1}{2}$ at. Acetone	.	.	.	.	.	C	3	H	3	O
1 at. Metacetone	.	.	.	.	.	C	6	H	5	O
3 at. Carbonic Acid	.	.	.	.	.	C	3			O ₆
1 at. Water	.	.	.	.	.			H		O
1 at. Anhydrous Sugar	.	.	.	.	.	C	12	H	9	O ₉

Metacetic Acid.—Gottlieb has shewn, that, when sugar is heated with 3 parts of fused potash, the metacetone and acetone which are formed in the first instance, as in the above-mentioned experiment, with lime, are oxidized in the second stage of the process with disengagement of hydrogen, the acetone yielding acetic and formic acids, which are partly further oxidized into oxalic acid, and the metacetone being converted into a new and remarkable acid, *metacetic acid*, the hydrate of which is $C_6H_5O_3.HO$, and which stands between acetic and butyric acids in the series of acids mentioned at p. 700, all the hydrates of which contain an equal number of atoms of carbon and hy-

drogen, always an even number, and 4 atoms of oxygen. The properties of this acid are also intermediate between those of acetic and butyric acids, its smell resembling that of butyric acid mixed with acrylic acid. It is not easily obtained pure, as the acetic acid, always present in the crude acid, forms salts so like those of metacetic acid, that it is hardly possible to separate them, except in the case of the salts which the acids form with soda, and even these are separated with difficulty.

Metacetic acid is interesting as the connecting link between acetic acid and the volatile oily acids belonging to the series above alluded to. Gottlieb has shown that it may be obtained by the oxidation of metacetone by means of bichromate of potash and sulphuric acid. It is here mixed with acetic acid, and carbonic acid is likewise formed in large quantity.

PRODUCTS OF THE OXIDATION OF SUGAR.

Saccharic Acid.—Formula, $C_{12}H_5O_{11} + 5HO = C_{12}H_{10}O_{16}$. (Thaulow.) It is a product of the action of dilute nitric acid on cane or grape sugar. Scheele confounded it with malic acid. More lately, Guérin Varry described it as oxalhydric acid; and it has been specially investigated by Erdmann, Hess, and Thaulow.

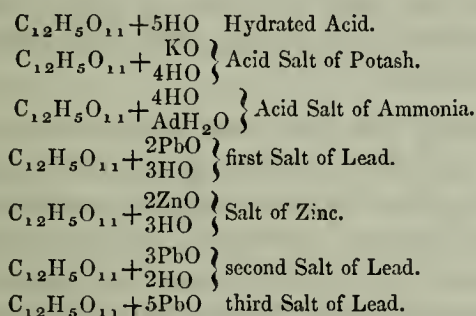
To obtain this acid, 1 part of sugar or gum is dissolved with the aid of heat in 2 parts of nitric acid diluted with 10 of water, and heat is applied as long as reaction takes place. After neutralizing the liquid by carbonate of lime, neutral acetate of lead is added. An abundant white precipitate is formed, which is decomposed by sulphuretted hydrogen. The acid liquid thus obtained is half neutralized with potash, and evaporated in the water-bath. After sufficient concentration, the liquid, if set aside, deposits crystals of acid saccharate of potash, which are decolorized by animal charcoal. The decolorized liquid is again crystallized, the crystals re-dissolved, re-precipitated by acetate of lead; and the precipitate, again decomposed by sulphuretted hydrogen, yields pure saccharic acid.

The diluted acid is a colourless slightly acid liquid; when concentrated it is syrupy, colourless, strongly acid, and by long standing it deposits colourless crystals. (Guérin.)

It forms flocculent white precipitates in lime and barytic water, which disappear on adding an excess of acid. It does not precipitate the salts of lime or baryta, nor even the nitrate of silver, until ammonia is added, when it forms a white precipitate which is reduced by the slightest heat. The metallic silver, as there is no effervescence,

attaches itself to the surface of the vessel, forming a bright mirror-like coating. Nitric acid, with the aid of heat, converts it into oxalic and carbonic acids. Heated with superoxide of manganese and sulphuric acid, it yields formic acid. Alkaline solutions added in excess, and heated with saccharic acid, give it a deep brown colour. It is soluble in alcohol in all proportions, not in ether. It dissolves zinc and iron, with disengagement of hydrogen. When kept in the diluted state it becomes mouldy.

Salts of Saccharic Acid.—This acid is very remarkable for the large number of compounds it forms with bases. It forms five series of salts, according as 1, 2, 3, 4, or five atoms of basic water contained in it are replaced by their equivalents of metallic oxides. The following table contains the saccharates the composition of which is known :—



If we add the elements of the basic water to those of the anhydrous acid, we find that the saccharic acid contains the elements of 1 atom of mucic acid, $\text{C}_{12}\text{H}_8\text{O}_{14} + 2\text{HO} = \text{C}_{12}\text{H}_{10}\text{O}_{16}$; that the first salt of lead and the salt of zinc have a composition identical, as far as the acid is concerned, with that of the mucate of silver, $\text{C}_{12}\text{H}_8\text{O}_{14} + 2\text{PbO} = 2(\text{C}_6\text{H}_4\text{O}_7 + \text{AgO})$, that is, the acids in these salts are isomeric or polymeric; and, finally, that in the third salt of lead the saccharic acid has the same composition as the citric acid in the citrate of silver; only the latter is combined with three atoms of base instead of five.

The production of two isomeric (or polymeric) acids, the saccharic and mucic, by the oxidation of two different substances, cane sugar and sugar of milk, which by fermentation yield the same products, appears likely to lead to the solution of the important problem which is still to be solved in regard to the constitution of these bodies, as well as of others, such as gum and starch, of which we hardly know more than the relative proportions of their elements.

The saccharates, although of the highest importance in reference to the theory of acids and salts, have little interest individually in their

properties, and need not here be described in detail. The existence of the third salt of lead above described, $C_{12}H_5O_{11} + 5PbO$, is one of the most convincing proofs of the existence of acids requiring more than one atom of base to form neutral salts. The oxide of lead here cannot be less than 5 atoms; because, if we reckon it 1, 2, 3, or 4, we shall have fractions of atoms in the composition of the acid. When, moreover, we observe in the two other salts of lead, that, for every atom of oxide of lead present, an atom of water has been eliminated, we cannot hesitate in considering the saccharic acid as a poly-basic acid (quinquebasic). To deny this, would lead to the admission of a different acid in each of the three salts of lead, and another in the salt of potash.

REMARKS ON THE CONSTITUTION OF THE COMPOUNDS OF THE DIFFERENT KINDS OF SUGAR, AND THE PRODUCTS OF THEIR DECOMPOSITION.

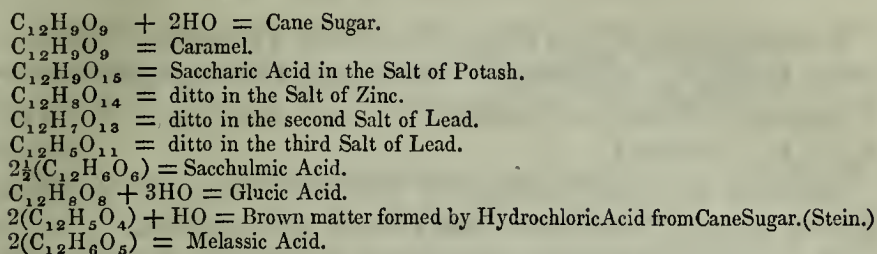
Notwithstanding the great analogy between cane sugar and grape sugar, both in their taste and in the properties of many of the products of their decomposition, we have only to consider their chemical characters, to be convinced that they are as distinct from each other as, for example, starch and woody fibre are from grape sugar.

Thus, the strong mineral acids, which hardly act on grape sugar, destroy cane sugar with facility: grape sugar, on the other hand, is instantly destroyed by alkalies; while cane sugar forms with lime, baryta, and oxide of lead, compounds of uniform composition which are permanent in the dry state.

Grape sugar produces, by the action of alkalies, a totally different series of compounds from those formed by cane sugar under the same circumstances. (Braconnot.) The phenomena which they exhibit in reference to polarized light are also quite different. (Biot.)

If they only differed by the amount of water contained in them in the hydratic state, their composition in the anhydrous state being the same, there would be no means of explaining such differences: moreover, if this were the case, it ought to be as easy to convert grape sugar into cane sugar as to do the reverse. In fact, however, these substances have nothing in common except the sweet taste, a property which they share with many other substances; the property of forming a definite compound with chloride of sodium; and, finally, the property of fermenting under certain circumstances, giving rise to the same products. But there is good reason to believe that cane sugar does not ferment till it has been converted into grape sugar.

The following table gives a view of the chief products of cane sugar and grape sugar:—



This table shows that 7 atoms of anhydrous sugar contain the elements of 1 atom of saccharic acid, 3 atoms of melassic acid, and 17 atoms of water; and that 2 atoms of saccharic acid contain the elements of 1 atom of melassic acid, 10 atoms of formic acid, and 4 atoms of oxalic acid. These considerations may help to explain the formation of melassic acid. At all events, it is not uninteresting to observe that saccharic acid contains the same number of atoms of carbon as sugar does, and seems to be formed from sugar as acetic acid is from alcohol.

When we compare the properties of the sugars above described with the processes followed in preparing them, we naturally conclude that such vegetable juices as contain free acids do not yield cane sugar when boiled or evaporated, but rather grape sugar, or uncrystallizable compounds of grape sugar with organic acids. Now cane sugar is converted into grape sugar by contact with sulphuric acid, and still more rapidly if heated with it. Again, the grape sugar, the formation of which cannot be prevented in the liquids from which cane sugar is extracted, is rapidly converted into glucic or melassic acid during the clarification of the juice by lime.

By the formation of glucic acid, 1 eq. of sugar disappears for each eq. of lime, and the molasses then contains glucate of lime. The juice of beet-root contains sea-salt and oxalate of potash. The sea-salt, in uniting with cane sugar, forms a compound which is deliquescent, and contains 6 parts of sugar for 1 of sea-salt; it remains in the mother-liquid as an uncrystallizable syrup. The lime decomposes the oxalate of potash; and the free potash, which the concentrated syrup now contains, converts part of the sugar, with the aid of heat, into melassic acid, which gives the syrup its brown colour.

Several manufacturers have proposed to neutralize the free alkali with sulphuric acid after the clarification by the milk of lime. This operation (Kodweiss, Ann. der Pharm.) agrees perfectly with theory, and has been confirmed by long experience.

SUGAR OF MILK, OR LACTINE.

Formula, $C_{24}H_{24}O_{24}$, or $C_{24}H_{19}O_{19} + 5HO$. (Berzelius.) Dried at 300° , $C_{24}H_{19}O_{19}$. (Berzelius.) Dried at 248° , $C_{24}H_{19}O_{19} + 3HO$. Formulæ of its compounds with oxide of lead, $C_{24}H_{19}O_{19} + 5PbO$ and $C_{24}H_{19}O_{19} + 10PbO$.

Bartholdi first described sugar of milk in 1619; up to the present time it has only been found in the milk of the mammalia.

It is obtained pure by evaporating whey till it crystallizes, and treating the crystals with animal charcoal and repeated crystallizations.

Sugar of milk crystallizes from its aqueous solutions in parallelepipeds, terminated by four-sided pyramids, which are white, semi-transparent, hard, crackling in the teeth, and assuming a foliated structure. Their sp. gr. is 1.543; they dissolve in 5 or 6 parts of cold water, and in $2\frac{1}{2}$ parts of boiling water, without forming a syrup. The crystals have a very feeble sweet taste, but the taste of a concentrated solution is much more decided.

When gently heated, first to 248° , and then to 284° , the crystals lose, without melting, 2 at. water, $= 5.3$ p. c.; but, if heated rapidly, they melt and lose 12.4 p. c. $= 5$ atoms of water. At 300° the melted liquid begins to turn yellow. (Berzelius.)

Sugar of milk is permanent in the air, loses no weight at 212° , and is insoluble in alcohol and ether. It is more soluble in acid and alkaline liquids than in pure water. It does not precipitate metallic solutions, and is not precipitated by infusion of galls.

Dilute mineral acids, such as sulphuric acid, or hydrochloric acid, convert sugar of milk, by a prolonged contact in the cold, and still more rapidly by boiling, into grape sugar. According to Vogel, the weight of the grape sugar produced is rather less than that of the sugar of milk employed. By calculation, 100 parts of sugar of milk, by combining with 2 at. of water, should produce 109.8 parts of grape sugar. The strong mineral acids, in acting on sugar of milk, produce the same substances, sacchulmine and sacchulmic acid, as are produced by cane sugar. When triturated with slaked lime and water, sugar of milk is dissolved with production of heat, and forms a brown liquid, from which alcohol precipitates a thick, bitter syrup, which attracts moisture from the air, and precipitates metallic solutions (Bouillon-Lagrange and Vogel); the alcohol dissolves acetate of potash. The relations between this liquid, sugar of milk, and glucic acid, have not been ascertained.

Nitric acid, with the aid of heat, converts sugar of milk into mucic acid; a part of this acid always passes into oxalic acid in the operation.

With the oxides of metals easily reducible, sugar of milk acts just as cane and grape sugar do. The higher degrees of oxidation are reduced to protoxides, or to the metallic state, while formic acid is produced.

The presence of sugar of milk in metallic solutions prevents the precipitation of the oxides by alkalies in many cases.

An aqueous solution of arsenic acid, when mixed with a solution of sugar of milk, acquires a reddish-brown colour after a short time.

Powdered sugar of milk absorbs ammoniacal gas (Berzelius), and hydrochloric acid (Bouillon-Lagrange and Vogel). It also combines with oxide of lead.

When milk is exposed to a temperature of from 95° to 104° , it undergoes the vinous fermentation; the sugar disappears, and alcohol is found in the liquid, while carbonic acid is disengaged during the whole fermentation. It is probable, however, that, before fermenting, the sugar of milk is converted into grape sugar; for the fermentation does not begin till the milk has curdled, that is, till an acid has been formed; and this acid may be the cause of the conversion of the sugar of milk into grape sugar. It has long been known that the curd of milk causes grape sugar to ferment. Since, therefore, the sugar of milk agrees with cane sugar in not fermenting until it has been converted into grape sugar, it has been thought advisable to describe it along with cane and grape sugar, the principal characters of which it possesses.

Sugar of Milk and Oxide of Lead.—A solution of sugar of milk, mixed with oxide of lead, becomes brown when boiled; but when the temperature does not exceed 140° , it remains colourless, and contains three different compounds. There is deposited at the bottom of the vessel a heavy granular powder, which becomes yellow and dried, and contains 87.2 p. c. = 10 at. oxide of lead. This is the basic compound. The liquid retains in suspension a white viscid compound, which, when dried, becomes yellowish and semi-transparent. It contains 63.729 p. c. = 5 at. oxide of lead, and is the neutral compound. Finally, the filtered liquid yields, on the addition of ammonia, an additional quantity of the neutral compound; and the liquid, evaporated to dryness, produces a transparent gummy mass, also becoming yellow when dried, and containing 18.12 p. c. oxide of lead. (Berzelius.)

PRODUCTS OF THE OXIDATION OF SUGAR OF MILK.

Mucic Acid.—Formula, $C_{12}H_{18}O_{14} + 2HO$. (Berzelius, Malaguti.) Symbol, $\overline{M} + 2 \text{ aq.}$ This acid was discovered by Scheele. It is formed by the action of dilute nitric acid on sugar of milk, gum, picromel, or mannite. One atom of crystallized sugar of milk, by taking up 12 at. oxygen, and losing 4 at. water, produces 2 at. crystallized mucic acid.

To obtain it, 1 part of gum or of sugar of milk is dissolved in 4 parts of nitric acid, sp. gr. 1.42, diluted with 1 part of water. Heat is applied till all effervescence has ceased; and, on cooling, the mucic acid is deposited. The acid from sugar of milk is always pure, while that from gum always contains mucate of lime, which is removed by neutralizing with an alkali and precipitating by an acid.

Mucic acid forms a white crystalline powder, which crackles in the teeth; its taste is feebly acid. It is soluble in 6 parts of boiling water, insoluble in alcohol, and very sparingly soluble in diluted acids. Its aqueous solution reddens litmus.

Mucic acid dissolves in oil of vitriol, giving to it a crimson colour. When this solution is heated, it is charred. It is probable that in the first instance a compound of the two acids is formed; for, on neutralizing the mixture with baryta, a considerable quantity of that base remains in solution. When the aqueous solution of mucic acid is evaporated by prolonged ebullition, the acid passes into the state of *modified mucic acid*.

When subjected to dry distillation, mucic acid blackens; and produces, among other substances, *pyromucic acid*.

SALTS OF MUCIC ACID.

Mucic acid neutralizes 2 equivalents of base, which are represented by 2 equivalents of a metallic oxide, or 1 eq. metallic oxide and 1 eq. water.

The alkaline mucates are soluble in water; those of the alkaline earths or of the heavy metallic oxides are insoluble. They are all decomposed by the mineral acids, which seize the base, and set free the mucic acid.

The mucate of silver contains 2 eq. oxide of silver, and forms a gelatinous precipitate. The formula of the mucate of lead is $\overline{M}, 2PbO + 2 \text{ aq.}$

With potash and soda, mucic acid forms 2 kinds of salt: in one

series, 1 atom of basic water is replaced by 1 at. of alkali; in the other, 2 at. basic water are replaced by 2 at. alkali. The composition of these salts, however, is little known.

Mucate of Ammonia.—Formula, $\overline{M}, 2AdH_4O$. It is prepared by supersaturating with carbonate of ammonia a hot solution of mucic acid. It crystallizes on cooling in flattened parallelopipeds, which are not decomposed by a new crystallization. This salt does not lose ammonia at 230° . (Malaguti.)

Mucate of Oxide of Ethyle.—Formula, $\overline{M}, 2AcO$, (Malaguti.) To prepare it, 1 part of mucic acid is dissolved in 4 parts of oil of vitriol with the aid of a gentle heat, and the solution allowed to cool. When it has become black, 4 parts of alcohol, sp. gr. 0.814, are added, and the mixture left to itself for twenty-four hours. During this time, it forms a white semi-solid mass, impregnated with a black acid liquid; the whole is placed on a porous brick and allowed to dry. The dry crystals are purified by solution in alcohol and re-crystallization.

The mucate of oxide of ethyle crystallizes in four-sided prisms, colourless and semi-transparent. Their sp. gr. is 1.17. They melt at 316° , and solidify again at 275° . At 338° they are resolved into alcohol, carbonic acid, acetic acid, pyromucic acid, and a residue of carbon. These crystals are sparingly soluble in cold water, but very soluble in boiling water; the solution has a bitter taste, and on cooling deposits rhombic prisms of the sp. gr. 1.32, melting at 316° and solidifying at 250° . These prisms are soluble in 2.27 parts of cold water, in 155 parts of cold alcohol, and more easily in hot water and alcohol. They are insoluble in ether.

The solution in water of mucate of oxide of ethyle is decomposed by boiling, especially when an alkaline base is added. The products of this decomposition are alcohol and mucic acid; the latter unites with the base.

Dry ammoniacal gas exercises no sensible action on the mucate of oxide of ethyle at temperatures below 338° ; but, if distilled in a current of ammonia, there is formed a very aromatic oil which dissolves in water, giving it a yellow colour. When this product is gently heated in a current of chlorine, it is converted into a yellow uncrystallized mass, very soluble in alcohol.

Modified Mucic Acid.—Laugier has observed that mucic acid acquires very different properties when its concentrated aqueous solution is boiled, or evaporated at a high temperature. It then leaves a residue slightly coloured, having much stronger acid properties than the mucic acid itself. This modified acid is much more soluble in cold water; it is soluble in alcohol, and it forms salts which have

different external characters from those of the mucates. By the spontaneous evaporation of its alcoholic solution it is obtained in square tables.

It is soluble in 17·2 parts of boiling water, and in 73 parts of cold water. When its boiling saturated solution is allowed to cool, it deposits crystals of ordinary mucic acid. Its salts are more soluble than those of the unaltered mucic acid. It is easily converted into ordinary mucic acid when dissolved in water, whether alone or in combination with bases.

When a saturated hot solution of modified mucic acid is saturated with ammonia, there is precipitated an insoluble salt containing the modified acid; while mucic acid, in the same circumstances, does not deposit crystals for some time. The modified acid, when distilled, yields the same products as the ordinary mucic acid.

Malaguti found both acids to contain equal proportions of the same elements. But the salt formed with oxide of silver by the modified acid yielded less silver than the mucate. The atomic weight of mucic acid is 1208·546, while that given by experiment for the modified acid is 1329 or 1320; this would indicate that the latter contained the elements of 1 atom of water more than the former. But as this salt of silver was not analysed so as to ascertain the composition of the acid it contained, the question of the identity in composition of the two acids remains for the present undecided.

Pyromucic Acid.—Formula, $C_{10}H_3O_5 + HO$. Symbol, $p\overline{M} + aq$. (Boussingault, Malaguti, Pelouze.) This acid was discovered by Scheele, who confounded it with benzoic acid. It is formed by the dry distillation of mucic acid. One at. mucic acid contains the elements of 1 at. pyromucic acid, 6 at. water, and 2 at. carbonic acid. $C_{12}H_8O_{14} + 2HO = C_{10}H_3O_5 + HO + 2CO_2 + 6HO$. To prepare it, the solid and liquid products of the distillation of mucic acid are first dried in the water-bath, and then sublimed at a temperature of from 265° to 284°. The yellowish sublimate is purified by solution and re-crystallization in water. It forms elongated tables, white and brilliant, melting at 265°, and subliming without residue at a temperature a little higher. It condenses in yellowish oily drops, which, on cooling, form a crystalline mass. It is permanent in the air, soluble in 26 parts of cold water, and in 4 parts of boiling water. The acid crystallized from water closely resembles benzoic acid, from which, however, it is distinguished by its greater solubility in cold water. It is easily soluble in alcohol, and is not changed by nitric acid.

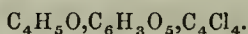
In its combinations with bases, its basic water is replaced by 1 eq. of base. The pyromucates of oxide of ethyle, of baryta, and of silver are

anhydrous. All the neutral pyromucates with metallic base are soluble in water. The alkaline pyromucates are very soluble. Some of them are also soluble in alcohol. The rest are less soluble and crystallizable. Subacetate of lead is precipitated by pyromucic acid.

Pyromucate of Oxide of Ethyle.—Formula, $\text{AeO}, \text{p}\overline{\text{M}}$. Discovered and analysed by Malaguti. It is obtained by distilling a mixture of 10 parts of pyromucic acid, 20 parts of alcohol, sp. gr. 0.814, and 5 parts of concentrated hydrochloric acid. The product is returned into the retort and distilled five times, and is then mixed with water; the new compound then separates in oily drops, which soon form a crystalline mass. The crystals are washed with water, and, after being dried, they are again distilled. The product which passes over at the end of the distillation is pure and anhydrous. It crystallizes in plates of four, six, and eight sides, derived from a rhomboidal prism, colourless, transparent, and unctuous to the touch. It has an odour like that of benzoic ether and also like naphthaline, and a pungent bitter taste, with an agreeable after-taste of anise and camphor. Its sp. gr. is 1.297; it melts at 94° , and boils between 406° and 412° . The density of its vapour is 4.859, representing four volumes. Calculation gives $\frac{19.455}{4} = 4.863$. It is sparingly soluble in water, soluble in alcohol and ether in all proportions. It does not inflame by contact with a burning body. By keeping, it gradually becomes coloured: ammonia does not change it, the fixed alkalies decompose it. The strong mineral acids dissolve it in the cold without change, but decompose it with the aid of heat.

In contact with chlorine gas, this body undergoes a peculiar change. It melts with disengagement of heat, without the production of hydrochloric acid or other gaseous products, and is found after the operation to have doubled its weight. When all excess of chlorine has been removed, there is obtained a colourless syrupy liquid, of a strong aromatic odour and a persistent bitter taste. Its sp. gr. is 1.496, and it is neutral to the test paper. When heated, it blackens, and gives off hydrochloric acid. It is very soluble in alcohol and ether. In water and in a moist air it becomes opaque and milky, being decomposed with formation of hydrochloric acid. This substance, which Malaguti, who discovered it, calls *Chloropyromucic Ether*, becomes hot when placed in contact with caustic potash; it then acquires colour, and deposits a curdy mass, which, with the aid of heat, is dissolved by the water. In this reaction the solution gives off vapours of alcohol; it becomes reddish-brown, and contains much chloride of potassium, but no pyromucic acid. When the chloropyromucic ether is mixed with alcohol previously saturated with ammonia, it blackens,

and is converted into sal-ammoniac and hydrocyanate of ammonia. Pyromucate of oxide of ethyle absorbs 4 eq. of chlorine to form the new ether, the empirical formula of which is $C_{14}H_8O_6Cl_4$. (Malaguti.) We have no positive data as to the arrangement of the elements in this compound; it appears, however, from the action of alkalies upon it, and the production of alcohol attending that reaction, that it is not the oxide of ethyle, but the pyromucic acid, which is acted on by the chlorine. According to Berzelius, it may be viewed as a mixture of pyrromucate of oxide of ethyle with subchloride of carbon, thus,



But the latest experiments of Malaguti do not confirm the constitution expressed by this formula.

Liebig has pointed out that pyromucic acid has the same formula and atomic weight as pyromeconic acid. But these acids are not identical.

MUSHROOM SUGAR.

By acting on the alcoholic extract of ergot of rye with water, Wiggers obtained a saccharine liquor, which, when evaporated to a syrup, yields quadrangular prisms, with a rhombic base, terminated by dihedrals, colourless, transparent, soluble in water and alcohol, insoluble in ether. This substance, in contact with yeast, undergoes the vinous fermentation. When the crystals are heated, they melt, and by a stronger heat are charred, giving out the odour of caramel. Nitric acid with the aid of heat converts them into oxalic acid.

When boiled with acetate of copper, this sugar does not precipitate any protoxide of copper: this is the only property by which it is distinguished from the other kinds of sugar.

Pelouze and Liebig, by the analysis of a small portion, not perfectly pure, obtained 38.3487 p. c. of carbon, and oxygen and hydrogen in the proportions to form water. These results are expressed exactly by the formula $C_{12}H_{13}O_{13}$; that is, the composition of grape sugar, minus 1 at. of water.

The substance described by Braconnot under the name of mushroom sugar is *mannite*, a substance which will shortly be described.

REMARKS ON THE NATURAL STATE AND FORMATION OF THE DIFFERENT SPECIES OF SUGAR.

Under the head of Grape Sugar we have mentioned several processes which prove that woody fibre and starch may be transformed into sugar, when subjected to the action of acids under certain conditions;

we have further shewn that sugar is produced by the contact of starch with malt; and, lastly, we have seen that salicine and phloridzine, by the action of acids, also yield grape sugar.

In like manner, amygdaline, under the influence of the white albuminous matter contained both in sweet and bitter almonds, and which has been called synaptase, is decomposed into several products, one of which is sugar. Salicine yields a similar result.

The active principle in malt, which produces the remarkable transformation of starch into grape sugar, is a substance which is not volatile, contains nitrogen, is tasteless, colourless, soluble in water, neutral to test paper, to which Payen and Persoz have given the name of *Diastase*. One part of diastase is sufficient to convert, in a few hours, 2000 parts of starch into sugar, provided the temperature do not exceed 158° . Diastase combines with no other substance; it is insoluble in absolute alcohol, soluble in weak alcohol. To obtain it, malt of the best quality is moistened and subjected to pressure; the juice is mixed with a little alcohol, which separates foreign matters, such as albumen; the filtered liquid contains diastase in solution.

In proportion as the diastase acts on starch, converting it into sugar, it disappears itself; and when the solution no longer acts on a fresh portion of starch, the presence of diastase cannot be detected in it. The reaction consequently is a purely chemical one, the careful study of which must certainly throw light on a multitude of the phenomena of vegetation.

The sugar formed during the germination of seeds containing starch, by the action of diastase, disappears at the same time that the woody fibre, forming the skeleton of the young plant, is developed.

Woody fibre (or lignine) and sugar differ from one another, for the same quantity of carbon, only in the proportion of the elements of water. For 12 atoms of carbon, anhydrous sugar contains 9 atoms, woody fibre 8 atoms, of water.

Woody fibre may be converted into grape sugar by the action of sulphuric acid; now, an inverse transformation seems to take place during the maturation of pulpy fruits, such as apples and pears, &c., as well as during the development of the germs of plants. In fact, previous to maturity, fruits are formed of a compact cellular tissue containing the elements of woody fibre, and filled with a liquid, containing very little sugar, a gummy substance, and a large quantity of free acid. During maturation, a part of the acid disappears by the influence of the oxygen of the air; the cellular tissue diminishes, and the proportion of sugar increases, insomuch that, instead of hard, woody, acid fruits, we obtain, if the maturation have been complete,

some weeks after they have been gathered, fruits which yield a sweet and syrupy juice, contained in a coriaceous envelope.

The shoots of a sparagus, as long as they have not risen above the surface of the soil, contain a large quantity of sugar; when acted on by light, they become green, and, as the colour deepens, the sugar disappears.

Sugar, like all the non-nitrogenized constituents of plants, is derived from the carbonic acid and water, which form the chief food of plants; 12 eqs. of carbonic acid $C_{12}O_{24}$, and 11 eqs. of water $H_{11}O_{11}$, contain the elements of cane sugar, $C_{12}H_{11}O_{11}$, and 24 eqs. of oxygen. But the change is a gradual one, formed of successive stages, in which compounds are first formed, which, like hydrated oxalic acid, contain less oxygen than carbonic acid and water do; then other still less oxygenated acids, such as malic, citric, and tartaric acids; and finally compounds in which there is only sufficient oxygen to form water with the hydrogen. This is, therefore, a process of deoxidation or reduction, which goes on in plants under the influence of light, and by which oxygen is given off and restored to the atmosphere in volume equal to the carbonic acid. In the following table the gradual diminution of oxygen may be traced:—

Carbonic Acid and Water, 12 eqs. of each,	$C_{12}H_{12}O_{36}$.
Oxalic Acid, hydrated, 6 eqs.	$C_{12}H_6O_{24}$.
Tartaric Acid	$C_{12}H_6O_{15}$.
Malic Acid	$C_{12}H_6O_{12}$.
Anhydrous Sugar	$C_{12}H_9O_9$.
Grape Sugar	$C_{12}H_{12}O_{12}$.

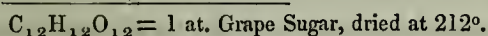
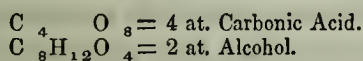
It will be observed that hydrated oxalic acid may be derived from carbonic acid $C_{12}O_{24}$, by the addition of 6 eqs. of water and the separation of 6 eqs. of oxygen; and that from hydrated oxalic acid, tartaric and malic acids may be formed by the separation of oxygen alone. Again, from malic acid, by the addition of 3 eqs. of water and the separation of 6 eqs. of oxygen, (or from tartaric acid by the addition of 3 eqs. of water, and the separation of 9 eqs. oxygen,) sugar may be formed. The characteristic phenomenon pervading all these changes in the living plant is the disengagement of oxygen, accompanied or not by the fixation of water. In the same way as sugar is formed, we can also see that starch, gum, woody fibre, and all bodies containing oxygen and hydrogen in the proportion to form water, may be derived from carbonic acid and water; and the function of the alkalis in plants seems to be to promote these changes, by aiding, through their affinity, the formation of the acids which occur in the earlier stages of the process. We shall return to this subject hereafter.

OF THE ALCOHOLIC OR VINOUS FERMENTATION.

This name is given to the peculiar decomposition which the different species of sugar undergo in certain circumstances; and by which their elements combine to form new compounds, which, under similar conditions, are always the same.

When a saccharine solution is placed in contact with substances in a state of decomposition or putrefaction, it is observed, after about twenty-four hours, if the temperature be kept between 38° and 86° , that the taste of the sugar has disappeared; pure carbonic acid is disengaged, and the liquid has acquired intoxicating properties. It now contains alcohol, which may be separated by distillation. If we compare the composition and quantity of these products with that of the sugar employed, we shall find them to contain the same weight of carbon.

Grape sugar, dried at 212° , contains the elements of 4 at. carbonic acid and 2 at. alcohol.



Hence, in fermentation, 1 atom of crystallized grape sugar, $= \text{C}_{12}\text{H}_{14}\text{O}_{14}$, must lose 2 at. water, and 100 parts of this sugar must yield 44.84 parts of carbonic acid, 47.12 parts alcohol, and 9.04 parts water. Guérin-Varry obtained, in two experiments, 10.572 of carbonic acid to 11.071 of alcohol, and 10.632 of carbonic acid to 11.166 of alcohol. The first experiment gives, for 44.84 of carbonic acid, 46.95 of alcohol: the second gives, for the same quantity of carbonic acid, 47.09 of alcohol. It follows from these results, that, in fermentation, sugar produces these new substances by a new grouping of its elements, without the elements of the body which excites the fermentation taking any share in the transformation.

According to the formula which we have adopted for crystallized cane sugar, that substance contains the elements of 4 at. carbonic acid, 2 at. oxide of ethyle, and 1 at. water: there are consequently required the elements of 1 at. water to enable it to yield the same products as 1 atom of dried grape sugar.

Very exact experiments have shewn that 100 parts of cane sugar give from 50.3 to 51.27 parts of carbonic acid, and 52.62 parts of alcohol. The sum of these products amounts to 103.89, that is, to more than the weight of the sugar fermented. This excess is found in the alcohol formed, as oxygen and hydrogen, in the proportions to form water.

It is, therefore, certain, that in the fermentation of cane sugar the elements of 1 at. water have a share in the transformation. One hundred parts of cane sugar and 5.025 parts of water ($C_{12}H_{11}O_{11} + HO$) produce, after fermentation,

51.298 Carbonic Acid,
and 53.727 Alcohol.

105.025.

Fermentation is nothing else but the putrefaction of a substance containing no nitrogen; that is to say, a metamorphosis by which the elements of a complex molecule group themselves, so as to form more intimate and more stable compounds, according to the special attractions of these elements. It is excited by the contact of all bodies, the elements of which are in a state of active decomposition. In nitrogenized substances of a very complex constitution, putrefaction (or fermentation) is spontaneously established when water is present, and when the temperature is sufficiently high, and it continues till the original compounds are wholly destroyed. Substances containing no nitrogen, on the contrary, require, in order to their undergoing this metamorphosis, the presence of a nitrogenized substance, already in a state of putrefaction (fermentation). The substances which best promote the change are gliadine, gluten, vegetable albumen, in short, all substances in a state of spontaneous decomposition, to which the general name of *ferment* is given. Putrefying animal substances are equally capable of exciting the same action.

Fermentation or putrefaction occurs only in complex organic molecules of a higher order. The reactions of these substances with the ordinary chemical agents show that the force which retains their elements in a state of combination is extremely feeble. Every substance which acts on them tends to cause their elements to assume a new arrangement, so that new products are formed, which, even in the same kind of decomposition, differ from each other in the case of different substances. We may assume that the molecules of the class of compounds to which the sugars belong are only retained in combination by virtue of the *vis inertiae* of their elements, and that every change in the equilibrium of these elements forces them to attract each other in a different order. Among the causes which disturb this equilibrium we must place the influence which the contact of a body undergoing spontaneous decomposition exercises on another compound susceptible of the same kind of decomposition.

Ferment, or yeast, is a substance in a state of putrefaction, the atoms of which are in a continual motion.

This motion, or conflict of the elements, communicating itself to

the sugar, destroys the equilibrium of its atoms. These no longer retain the same arrangement, and group themselves according to their special attractions. The carbon of the sugar is divided between the hydrogen and the oxygen: there is formed, on the one hand, a carbonized compound, containing almost all the oxygen (carbonic acid); and, on the other, a second carbonized compound, containing all the hydrogen (alcohol). This kind of decomposition is the same for all organic substances which putrefy, or undergo a metamorphosis; it being understood that the products vary according to the composition of these substances.

It is highly probable that cane sugar, before it undergoes the vinous fermentation, is converted into grape sugar by contact with the ferment; and that consequently it is grape sugar alone which yields alcohol and carbonic acid.

We have classed lactine with the sugars, on account of the indisputable fact, that this substance disappears in milk exposed to a proper temperature with the same phenomena as characterize the fermentation of the other sugars. In this case, also, carbonic acid is disengaged, and alcohol left in the liquid.

It is therefore probable, if not certain, that the lactine is converted into grape sugar before giving rise to these products; for milk does not ferment until it be sour, and, when the fermentation is over, there is found in the liquid a large quantity of an organic acid. Now, we know that lactine, by the action of many acids, is converted into grape sugar; and it is natural to conclude that the same transformation occurs before, or during, the fermentation of milk.

In the fermentation of vegetable juices containing sugar, it appears that the elements of certain other principles therein dissolved take an essential part in the formation of the new products occasioned by the action of the air on the juice of the grape, of fruits, and of other plants.

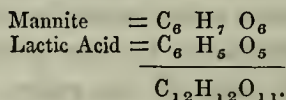
The nitrogenized matters in solution, such as gluten, gliadine, vegetable albumen, &c., are spontaneously decomposed; and it is then that the decomposition of the sugar is commenced, and continues till the sugar has entirely disappeared. When the juice has once begun to ferment, it may be preserved from the contact of the atmosphere, without the action being thereby arrested. The nitrogenized matters of the juice are constantly precipitated in the shape of ferment or yeast; and in the fermented liquors, besides alcohol, there are found other substances, such as cenanthic ether, oil of potato, oil of grain, &c., the presence of which could not be detected previous to fermentation. These latter are possibly the products of the action of the

nitrogenized matters of the juices on the sugar they contained ; but it is also possible, and even probable, that they may be the products of a peculiar transformation of the sugar itself, going on at the same time with the vinous fermentation.

With regard to the phenomenon commonly termed viscous or mucilaginous fermentation, it is certainly the result of the reciprocal action of the substances held in solution in the vegetable juices. Mannite, gum, and lactic acid are the principal products of this reaction.

OF THE VISCOUS FERMENTATION.

When the juice of beet-root, of carrots, of onions, and other saccharine vegetables, is exposed to a temperature of from 86° to 104° , a brisk effervescence is observed ; cane sugar is transformed into grape sugar, carbonic acid is disengaged, and when the action is over, all the sugar has disappeared. The liquid contains merely traces of alcohol ; but, on the other hand, a large quantity of mannite and of lactic acid. Besides these, there is found a substance which is precipitated by alcohol in the shape of a syrupy mucilage, (hence the term viscous or mucilaginous fermentation,) very thick, and possessing exactly the composition of gum arabic. All these substances seem to be the result of the action of the nitrogenized or albuminous principles of the juice on the sugar. With the exception of ammonia, no other nitrogenized substance can be discovered in the fermented liquor. Now, gum arabic, or a substance of the same composition, contains exactly the elements of cane sugar ; and mannite, *plus* lactic acid, contains the elements of dried grape sugar, *minus* 1 at. oxygen.



It is, therefore, possible that these two substances are formed by a deoxidation of sugar, 1 at. of oxygen from which combines with the elements of the nitrogenized substances.

To excite the viscous fermentation in pure sugar, it is dissolved in 20 parts of water which has previously been boiled with the yeast of beer free from starch, or with gluten ; the solution is then left in a temperature of 86° to 104° . (Desfosses, Pelouze.) Sulphuric acid, infusion of nut-galls, and many other substances prevent this decomposition.

It has lately been shewn that when cane sugar, grape sugar, or lactine is made to ferment by contact with decaying caseine and chalk, a very large quantity of lactic acid is formed, which combines

with the lime of the chalk; but it is not fully ascertained whether this fermentation is the same as the viscous fermentation.

On account of the connexion of lactic acid and mannite with sugar, the history of these substances is here subjoined.

MANNITE.

Formula, $C_6H_7O_6$. It is named from manna, of which it forms the greater part. It is also found in the juices which exude from several species of cherry and apple, in various mushrooms, in some roots, such as that of celery; in the fermented juice of beet-root, carrots, onions, &c.; and it is also obtained in small quantity when starch is transformed into grape sugar by boiling with diluted sulphuric acid. It is easily purified by solution in boiling alcohol, which on cooling deposits almost the whole of it in fine radiated groups of crystals. These are quadrangular prisms, anhydrous, colourless, transparent, of a silky lustre. From water it crystallizes in very large anhydrous prisms. It has a faint sweetish taste, is very soluble in water and hot alcohol, sparingly soluble in cold alcohol. Its aqueous solution cannot be made to undergo the vinous fermentation.

Mannite melts, without loss of weight, into a colourless liquid, which, on cooling, forms a crystalline mass. Nitric acid converts it into oxalic and saccharic acids, not into mucic acid. Hypermanganate of potash converts it into oxalate of potash. Concentrated arsenic acid gives it a brick-red colour. Its aqueous solution dissolves oxide of lead.

LACTIC ACID.

Formula of the acid in the lactate of zinc, $C_6H_5O_5$. Symbol, $\bar{L}$; hydrated acid, $C_6H_5O_5 + aq. = \bar{L}, aq.$; sublimed acid, $C_6H_4O_4$.

Lactic acid was discovered by Scheele in whey. Braconnot also described it under the name of Nancéic acid. It was found by Berzelius in several animal liquids, and particularly in human urine. (Henry.) It is formed in milk when it becomes sour, in the fermentation of several vegetable juices, as well as in that of sugar in contact with caseine, and in the putrefaction of some animal matters. The acid which is found in the fermented juice of beet-root, turnips, and carrots, in sour-kraut, in fermented rice-water, in the fermented extract of nux vomica, and in the infusion of bark used by tanners, is for the most part pure lactic acid. Liebig, who denies the existence of lactic acid in the urine, has lately discovered it in the juices of animal flesh.

To obtain lactic acid, the lactate of baryta is dissolved in water, and the baryta separated by dilute sulphuric acid, avoiding excess. The liquid filtered from the sulphate of baryta is evaporated in vacuo along with sulphuric acid, assisting the evaporation with a gentle heat. In this way is obtained the hydrated acid, which is further purified by being dissolved in ether, the solution filtered, and the ether removed by evaporation.

The hydrated lactic acid is a colourless syrupy liquid; its sp. gr. is 1.215 at 68°. It has a very strong acid taste, which is remarkably weakened by diluting the acid. It attracts moisture from the air. At 266° it loses 1 eq. of water, leaving the anhydrous acid, $C_6H_5O_5$. This, when further heated to 480°, yields a crystalline sublimate, which has been called *sublimed* or *concrete lactic acid*, or *lactide*. The greater part of the acid is converted into this new body, which sublimes in shining white crystals: they are purified by pressure in bibulous paper, and solution in boiling alcohol. On cooling, the new acid is deposited in rhomboidal tables of dazzling whiteness, fusible at 225°, volatile at 480°, yielding white, inflammable, acrid vapours. These crystals have a weak acid taste, dissolve slowly in cold water, but are quickly dissolved in hot water, and attract moisture from the air. The solution yields by evaporation a thick syrup, which has all the properties as well as the composition of the hydrated acid above described. No crystals can be obtained from this solution. That which is most remarkable in this body is its composition, which is expressed by the formula $C_6H_4O_4$: it is, therefore, distinguished from the hydrated acid by containing 2 at. of water less, which sufficiently explains its mode of formation. The conversion of its solution, moreover, into hydrated acid by evaporation, proves the accuracy of the above formula.

Lactide, when exposed to ammoniacal gas, absorbs it with avidity, forming a new compound, *lactamide*: $C_6H_4O_4 + NH_3 = C_6NH_7O_4$. This body may be viewed as derived from anhydrous lactic acid and ammonia by the separation of water; $C_6H_5O_5 + NH_3 = HO + C_6NH_7O_4$. It is remarkable as having the same empirical formula with two other compounds, namely, carbamate of oxide of ethyle (urethane), $C_4H_5O + CO_2$, $CONH_2$, and sarcosine, a new base very recently discovered by Liebig among the products of decomposition of kreatine, a compound occurring in the juices of muscular flesh.

Lactic acid dissolves a very large quantity of freshly precipitated phosphate of lime, and coagulates albumen; it dissolves in cold milk without changing it, but coagulates it when the mixture is boiled.

LACTATES.

In the neutral lactates, the hydratic water of the acid is replaced by 1 eq. of metallic oxide. No acid lactates are known; but it appears that there exist basic lactates, which have not been studied. The general formula for the neutral lactates is $\bar{L},MO$. They are all soluble in water; but Braconnot employed the lactate of zinc, on account of its sparing solubility, to obtain a lactate free from foreign salts.

Lactate of Urea.—Formula, $\bar{L},C_2N_2H_4O_2$. (Cap and Henry.) Discovered in human urine by these chemists. This compound may be obtained directly by double decomposition from the lactate of lime and the oxalate of urea. The liquid filtered from the oxalate of lime is evaporated at a gentle heat, and crystallized in vacuo near sulphuric acid.

To extract it from urine, the urine is evaporated to the consistence of syrup, the free acid is neutralized by chalk, and filtered to separate the salts which have been deposited on cooling. The filtered liquid is dried in the water-bath, and the residue digested in a gentle heat with a mixture of 2 parts alcohol and 1 part ether. The lactate of urea dissolves in this liquid, and is obtained by evaporation in yellowish prisms, which may be rendered colourless by charcoal and by repeated crystallization.

The lactate of urea crystallizes in hexagonal prisms, which have a pungent and cooling taste, and attract moisture from the air. When moderately heated, it melts and volatilizes without change. When strongly heated it is decomposed, and leaves a carbonaceous residue. According to Cap and Henry, the lactate of urea is distinguished from the oxalate and nitrate of urea by this, that the latter contains 1 at. of combined water, which is not found in the former.

According to Gregory, whose observations are confirmed by several other chemists, the process of Cap and Henry yields pure urea, and it is even doubtful if the lactate of urea exist.

The *Lactates of Ammonia, Potash, and Soda* are deliquescent, and do not crystallize.

The *Lactate of Baryta* is obtained by precipitating the lactate of zinc by baryta. It is very soluble in water, and when dry forms a semi-transparent amorphous mass. It is used in the preparation of lactic acid.

Lactate of Lime.—According to Corriol, the nux vomica contains this salt ready formed. It is obtained by making an aqueous infusion of nux vomica, evaporating to the consistence of syrup, and acting on the residue with boiling alcohol, which dissolves the lactate of lime. The alcohol is distilled off: after some time, the concentrated solution

deposits the salt in the form of small granular crystals, which are purified by means of charcoal and re-crystallization. *Nux vomica* contains 2 to 3 p. c. of lactate of lime.

This salt is easily obtained from sour whey, by evaporating it to the consistence of syrup, treating the residue with alcohol, and saturating the alcoholic solution with milk of lime or with chalk. The alcohol is then distilled off, and the residue dissolved in a little water, and crystallized. (Henry.)

But the easiest and best method of obtaining lactate of lime is to cause a solution of sugar in about five parts of water to ferment by the addition of pressed curd or pure cheese, at a temperature of from 90° to 100° F., adding prepared chalk to neutralize the acid as it is formed. In a variable time, depending on the state of the caseine and the temperature, the whole mass becomes nearly solid, from the separation of crystalline grains of lactate of lime, which is purified by solution in hot water and re-crystallization. The liquid strained from the lactate of lime probably contains mucilage, and certainly often yields mannite, but in a quantity so small, when compared with that of the lactate, that it is doubtful whether this fermentation be the viscous, and not rather a peculiar one, the chief product of which is lactic acid. It is easy to see how sugar may yield lactic acid, without any other product, since 1 eq. of grape sugar $C_{12}H_{12}O_{12}$, or 1 eq. cane sugar, $C_{12}H_{11}O_{11}$ + 1 eq. water, is exactly equal to 2 eq. of hydrated lactic acid, $2(C_6H_6O_6)$. Recent researches tend to show that the latter view is correct, and that lactic acid is the sole product of a peculiar fermentation, which may be called the *lactic fermentation*.

The lactate of lime crystallizes in colourless needles, grouped round a common centre: they are more soluble in hot than in cold water, and contain $29.5 = 5$ at. water of crystallization, which is expelled when the salt is heated so that it melts.

Lactate of Zinc.—The best method of obtaining this salt is to exhaust sour-kraut with boiling water, and to neutralize the decoction with carbonate of zinc. The filtered liquid is then evaporated to the consistence of syrup, and the crystals which form are decolorized by charcoal and by repeated crystallizations. The salt may also be obtained from sour whey, by proceeding as directed for lactate of lime, substituting carbonate of zinc for chalk.

Lactate of zinc crystallizes by the cooling of a hot solution in four-sided prisms terminated by obliquely truncated summits: they contain 3 at. of water. Alcohol added to the watery solution causes the deposition of a basic salt, which is soluble and crystallizable: it appears to contain 3 at. oxide of zinc, but this requires confirmation.

Lactate of Protoxide of Iron is a sparingly soluble, nearly colourless salt, which has lately been employed in medicine.

The *Lactates of Alumina, Nickel, Lead, and Mercury* are very soluble in water, and do not crystallize.

The *Lactate of Magnesia* crystallizes in small plates containing 3 at. water, and requires 30 parts of cold water to dissolve it.

The *Lactates of Protoxide of Iron*, ($\bar{L}, \text{FeO}, 3 \text{ aq.}$), of *Oxide of Copper*, ($\bar{L}, \text{CuO}, 2 \text{ aq.}$), and of *Silver* are crystallizable.

BUTYRIC FERMENTATION.

When sugar has been converted into lactate of lime, as described under that salt, by the action of caseine in contact with chalk, if, instead of separating the lactate, it be kept in contact with the caseous ferment at a temperature of from 100° to 105° , the sparingly soluble lactate of lime gradually dissolves, and after a shorter or longer time entirely disappears, butyrate of lime, a much more soluble salt, being found in its place. This change is said to be accompanied with the disengagement of carbonic acid and hydrogen; but it has not yet been fully investigated. It is certain that in this way butyrate of lime may be formed in any desired quantity. Now, hydrated butyric acid is $\text{C}_8\text{H}_8\text{O}_4$, while hydrated lactic acid is $\text{C}_6\text{H}_6\text{O}_6$; and therefore we must suppose 1 eq. of butyric acid to be derived from 2 eqs. of lactic acid, $\text{C}_{12}\text{H}_{12}\text{O}_{12}$; the difference is $\text{C}_4\text{H}_4\text{O}_8$, that is, 4 eqs. of carbonic acid and 4 eqs. of hydrogen. This is on the supposition, which appears probable, that the lactic acid is the sole source of the butyric acid, and also, that lactic acid is the chief or only product of the formation of sugar in contact with caseine. If that fermentation be, however, the true viscous fermentation, producing mannite and mucilage, then these substances may also contribute to the formation of butyric acid. All these questions demand a full and minute investigation; but the result of the latest researches is such as to render it highly probable that butyric acid, carbonic acid, and hydrogen are the only products of the butyric fermentation.

In the meantime, the undoubted fact that butyric acid may be formed artificially from sugar, is of the utmost importance, inasmuch as butyric acid is also formed in the body of the cow and other animals, no doubt from the sugar or starch of their food, being found in butter, along with other analogous volatile oily acids, which have not yet been artificially formed from sugar. It is plain that we have here a principle which, when fully investigated, will lead to the artificial production of oily or fatty matters in general, since, as has been shewn by

Liebig and others, these are certainly, in part at least, formed from sugar in the animal organism, and can only be so formed by a separation of oxygen, whether free or combined with hydrogen and carbon, from the elements of sugar. We shall see, under the head of Amyle, that another of the volatile oily acids, the next, indeed, in the series (at p. 700) to butyric acid, namely Valerianic acid, has also been formed artificially from oil of potato spirit, a substance produced in abundance during the vinous fermentation of the grape sugar made from potato starch.

METHYLE.

Formula, C_2H_3 . Symbol, Me.

The name of Methyle has been given to the hypothetical radical of pyroxylic spirit and its combinations; it is analogous to ethyle in its chemical characters, but differs essentially from it in composition.

The compounds of methyle with oxygen, chlorine, bromine, and iodine are formed by acting on the hydrate of oxide of methyle with sulphuric acid, and the corresponding hydracids of chlorine, bromine, and iodine.

All the compounds of methyle are obtained from the *pyroxylic spirit*, which was first discovered by Philip Taylor among the products of the dry distillation of wood. But it has recently been ascertained that oxide of methyle is also a natural product, since the oil of Wintergreen (*Gaultheria procumbens*) is nearly pure salicylate of oxide of methyle.

It is to the important researches of Dumas and Peligot that we owe the knowledge of its composition, its chemical nature, and the various compounds which it forms. Most of the following details are taken from the memoir of these chemists. (Ann. de Chimie, vol. lviii. p. 5.)

OXIDE OF METHYLE.

Syn. Hydrate of Methylene; Methylic Ether.—Formula, $C_2H_3O = MeO$. (Dumas and Peligot, Kane.)—It is prepared by distilling together equal volumes of oil of vitriol and pyroxylic spirit. The gases disengaged are made to pass first through milk of lime, and then through several bottles of pure water, which absorbs the oxide of methyle. When this aqueous solution is gently heated, it gives off the oxide of methyle, which may be collected over mercury. It is deprived of moisture and of pyroxylic spirit by the contact of caustic potash.

It is a colourless gas, having a very agreeable ethereal odour; it is very inflammable, and burns with a pale blue flame. It is not lique-

fied by a cold of 4° . It is dissolved by water, to which it gives an ethereal odour and a pungent taste. One volume of water absorbs 37 volumes of the gas. It is much more soluble in alcohol, also in pyroxylic spirit, and in oil of vitriol: the latter separates from it when water is added.

When this gas and the vapour of anhydrous sulphuric acid are mixed in a vessel carefully cooled, they unite to form the neutral sulphate of oxide of methyle. (Regnault.)

By combining with oxygen acids, the oxide of methyle forms neutral and acid salts. It contains the same elements as alcohol, united in the same proportions; but its molecule is only half as large, and the density of its vapour is 1.605, which represents 2 volumes, while that of alcohol represents 4 volumes. The calculated density of oxide of methyle is $\frac{3 \cdot 1403}{2} = 1 \cdot 570$.

HYDRATE OF OXIDE OF METHYLE.

Syn. Pyroxylic Spirit; Bihydrate of Methylene.—Formula, C_2H_3O , aq. = MeO , aq.

The pyroxylic spirit of commerce is very impure; it contains, besides the hydrate of oxide of methyle, which forms the chief part of it, acetone and other inflammable liquids.

To purify it, we avail ourselves of the property which it has of forming a compound with chloride of calcium, which is with difficulty decomposed by a heat of 212° . The raw spirit is introduced into a retort with an excess of chloride of calcium, and the mixture is distilled in the water-bath as long as volatile matter passes off. A quantity of water equal to the spirit employed is then added, and the distillation is continued. The product is now pure pyroxylic spirit, carrying along with it a little water, which is removed by a second distillation with quicklime. It sometimes happens that the first drops of hydrate of oxide of methyle which pass become turbid on the addition of water. In this case the receiver must be changed.

Pure pyroxylic spirit is a very mobile, colourless liquid, having a peculiar empyreumatic odour, resembling at the same time that of alcohol and that of acetic ether. It is very inflammable, and burns with a pale flame. It mixes perfectly with water, also with alcohol and ether, and is neutral to test paper. It boils at about 150° ; its sp. gr. at 68° is 0.798. The density of its vapour is 1.120, representing 4 volumes. Calculation gives $\frac{4 \cdot 4411}{4} = 1 \cdot 11$.

When the hydrate of oxide of methyle is distilled with hyperoxide of manganese and sulphuric acid, or when its vapour is brought

into contact with the powder of platinum and the air, a series of oxidized products is obtained, among which are observed *formic acid*, *formomethylal*, and *methylal*.

An excess of nitric acid, with the aid of heat, converts the pyroxylic spirit into water and oxalic acid. By adding nitrate of silver to the mixture, and evaporating so as to expel the nitric acid, we obtain a white residue of oxalate of silver. Chlorine decomposes pyroxylic spirit with facility, giving rise to a variety of products containing chlorine.

In contact with potassium, pyroxylic spirit disengages pure hydrogen; there is formed a compound of potash with oxide of methyle, which remains in solution. (Böckmann.)

The hydrate of oxide of methyle dissolves small quantities of sulphur and phosphorus with the aid of heat; it also dissolves many resins. It mixes with most essential oils; and forms crystalline compounds with baryta, lime, and chloride of calcium.

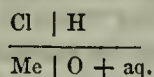
Hydrate of Oxide of Methyle and Baryta.—Formula, $\text{MeO}, \text{aq.} + \text{BaO}$. (Dumas.) Pure baryta dissolves easily in pyroxylic spirit, with the evolution of much heat; the solution becomes brown when exposed to the air. Evaporated in vacuo, it deposits silky needles, fusible when heated. When calcined, they leave a residue of carbonate of baryta and carbon. When the heat is first applied, pyroxylic spirit is given off; afterwards an oily liquid passes over. According to Dumas and Peligot, the crystals contain 70.5 p. c. of baryta, whence they deduce the above formula.

Hydrate of Oxide of Methyle and Chloride of Calcium.—Formula, $2(\text{MeO}, \text{aq.}) + \text{CaCl}$. (Kane.) The hydrate of oxide of methyle dissolves chloride of calcium with great facility, becoming hot if the solution is concentrated; it forms, on cooling, a crystalline mass; if less concentrated, it forms large six-sided tables, deliquescent in a moist atmosphere. When dried in vacuo over sulphuric acid, they leave, when calcined, a residue of 46.7 p. c. of chloride of calcium. Water decomposes this compound, separating the pyroxylic spirit.

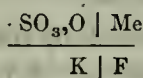
COMPOUNDS OF METHYLE WITH THE NEGATIVE NON-METALLIC BODIES, AND WITH SULPHUR.

The compounds of methyle with chlorine, bromine, and iodine may be obtained, either directly by the action of a hydracid on the hydrate of oxide of methyle, or by distilling the sulphate of oxide of methyle with the corresponding haloid salt. In the former case, the oxygen of the oxide of methyle combines with the hydrogen of the hydracid, forming water, while the negative element of the hydracid takes its

placc. Thus, for example, hydrochloric acid, acting on hydrate of oxide of methyle, gives chloride of methyle and 2 eq. water:—



In the latter case, the metal of the haloid salt is oxidized at the expense of the oxide of methyle, forming a metallic oxide, which in its turn combines with sulphuric acid, while the negative element of the salt combines with the methyle which is set free. Thus, when sulphate of oxide of methyle acts on fluoride of potassium, there are formed sulphate of potash and fluoride of methyle:—



The compounds of methyle with chlorine, bromine, &c. are neutral to test paper. Water does not affect them, and an aqueous solution of a caustic alkali decomposes them with much difficulty. On the other hand, a solution of caustic alkali in alcohol, or pyroxylic spirit, readily converts them into haloid salts and hydrate of oxide of methyle. Metallic solutions cannot detect the chlorine, bromine, &c. in the solutions of these compounds in alcohol or pyroxylic spirit.

These compounds are very inflammable; the hydracid of the negative element is a constant product of their combustion. Thus, chloride of methyle, in burning, gives off hydrochloric acid. When they are passed through a red-hot tube, they are resolved into the hydracid, gaseous carbo-hydrogens, and a residue of carbon.

Chloride of Methyle. *Syn. Hydrochlorate of Methylene.*—Formula, $\text{C}_2\text{H}_3 + \text{Cl} = \text{MeCl}$. (Dumas and Peligot.) This compound is best obtained by distilling sulphate of oxide of methyle with chloride of sodium; or by heating a mixture of common salt, sulphuric acid, and pyroxylic spirit. The product is collected under water, which retains sulphurous acid, pyroxylic spirit, and oxide of methyle, if any should accidentally be disengaged. The chloride of methyle is a colourless gas, having an ethereal odour and a sweet taste. Water at 60° dissolves 2.8 times its volume under the ordinary pressure. It burns with a white flame edged with green. Its sp. gr. is 1.7378, representing 4 volumes. The calculated density is $\frac{6.9189}{4} = 1.729$. It is not liquefied by a cold of 0° .

According to Regnault, chlorine, aided by the direct rays of the sun, decomposes this substance, forming hydrochloric acid and several new compounds containing chlorine. (See below, “Combinations of Formyle with Chlorine,” and “Action of Chlorine, &c. on Methyle.”)

Iodide of Methyle.—Formula, MeI . (Dumas and Peligot.) It is

prepared by distilling a mixture of 12 to 15 parts of pyroxylic spirit, 8 parts of iodine, and 1 part of phosphorus; the latter added by degrees in fragments. By adding water to the product, the iodide is at once separated: it is purified by redistillation along with chloride of calcium and oxide of lead. It is a colourless liquid, burning with difficulty. It boils between 104° and 122° : its density at 70° is 2.237.

Fluoride of Methyle.—Formula, MeF . (Dumas and Peligot.) Obtained by distilling sulphate of oxide of methyle with fluoride of potassium. It is a colourless gas, having a pleasant ethereal odour: its density is 1.186. It is inflammable, and burns with a blue flame. Water absorbs 1.5 time its volume.

Cyanide of Methyle.—Obtained by distilling sulphate of oxide of methyle with cyanide of potassium. An ethereal liquid, of an alliaceous odour, insoluble in water. (Dumas and Peligot.)

Sulphuret of Methyle.—Formula, $\text{C}_2\text{H}_3\text{S} = \text{MeS}$. (Regnault.) It is easily obtained by the action of chloride of methyle on an alcoholic solution of protosulphuret of potassium. The latter is placed in a tubulated retort furnished with an adapter and a receiver. A current of chloride of methyle is introduced by the tubulure; and, when the solution is saturated with it, a gentle heat is applied to the retort, while the current of chloride of methyle is continued. A volatile liquid condenses in the receiver, which must be carefully cooled. It is washed several times with water, and rectified with chloride of calcium. When an alkaline sulphuret is distilled with the sulphate of oxide of methyle, there is also obtained an ethereal liquid of a disagreeable alliaceous smell, which appears to be nothing else than sulphuret of methyle. (Dumas and Peligot.) The sulphuret of methyle is a very mobile liquid, having a very offensive smell. Its density is 0.845 at 70° ; it boils at 106° . The density of its vapour has been found to be 2.115, representing 2 volumes. The calculated density is $\frac{4.3164}{2} = 2.158$. (Regnault.) Chlorine acts energetically on this compound, producing several new substances. (See below, "Products of the Decomposition of Methyle, and the Substances derived from it.")

Hydrosulphuret of Sulphuret of Methyle.—When heat is applied to a mixture of the double sulphate of potash and oxide of methyle with the hydrosulphuret of sulphuret of potassium, an extremely volatile liquid is obtained, having an alliaceous odour very similar to that of the corresponding compound of ethyle (mercaptan), but more resembling the smell of leeks than that of onions. It is a colourless liquid, lighter than water; it boils at 70° , and acts like mercaptan on the oxides of lead and mercury. The compound with mercury crystallizes from alcohol in brilliant white scales, which do not melt at 212° . (W. Gregory.)

OXYGEN SALTS OF METHYLE.

The oxide of methyle, by combining with the oxygen acids, produces neutral and acid salts. In the neutral salts, the hydratic water of the acid is replaced by 1 eq. of oxide of methyle. The acid salts contain 1 eq. of neutral salt and 1 eq. of the hydrated acid.

These salts exhibit, with the metallic salts, the same reactions as the salts of oxide of ethyle; thus, knowing the history of the latter, it is easy to deduce that of the compounds of oxide of methyle.

The anhydrous metallic oxides have no action on them, while the hydrated alkalies decompose them with great facility. Löwig had stated that in this case no hydrate of oxide of methyle is formed; but the experiments of Malaguti and Böckmann have proved that this assertion is altogether erroneous.

Neutral Sulphate of Oxide of Methyle. *Syn. Sulphate of Methylene.*—Formula, MeO, SO_3 . (Dumas and Peligot.) When concentrated sulphuric acid is mixed with pyroxylic spirit, a reaction takes place similar to that between the same acid and alcohol; that is to say, there is formed bisulphate of oxide of methyle, which, when heated, is resolved into sulphurous acid, carbon, oxide of methyle, and neutral sulphate of oxide of methyle. The quantity of the latter increases as we increase the proportion of sulphuric acid. All the other phenomena in this reaction are the same as in the action of sulphuric acid on alcohol. It has been already mentioned that the gaseous oxide of methyle combines directly with anhydrous sulphuric acid to produce the neutral sulphate.

To obtain this compound, 1 part of pyroxylic spirit is distilled with 8 or 10 parts of oil of vitriol. The neutral sulphate collects in the receiver as an oily liquid. It is washed with cold water to remove the acid, dried by means of chloride of calcium, and rectified with quicklime to remove sulphurous acid.

It is a colourless liquid, having an alliaceous smell. Its sp. gr. is 1.324 at 70°. It boils at 370°, and distils unchanged. The density of its vapour is 4.3634; hence it is composed of equal volumes of anhydrous sulphuric acid, and of oxide of methyle condensed into 1 volume.

It is slowly decomposed by cold water, forming bisulphate of oxide of methyle and hydrate of oxide of methyle. It is not changed by being heated with anhydrous alkalies or metallic oxides; but the hydrated alkalies quickly decompose it, forming hydrate of oxide of methyle, and a double sulphate of the alkali with oxide of methyle.

Heated with a metallic chloride, cyanide, &c., or with an alkaline benzoate, succinate, &c., it yields chloride or cyanide, &c. of methyle, or benzoate, succinate, &c. of oxide of methyle; and these products, being volatile, pass into the receiver.

By ammonia, dry or dissolved, it is acted on, producing *Sulphamethylan*.

The neutral sulphate may be employed to yield all the other compounds of oxide of methyle.

Bisulphate of Oxide of Methyle. Syn. Sulphomethylic Acid.—Formula, $\text{MeO}, \text{aq.}, 2\text{SO}_3$. This compound is formed when sulphuric acid is mixed with pyroxylic spirit, or when the neutral sulphate is boiled with water. It was discovered at the same time by Dumas and Peligot, and by Kane. It is easily obtained by cautiously adding diluted sulphuric acid to a solution of the double sulphate of baryta and oxide of methyle. The filtered liquid is evaporated in vacuo over sulphuric acid. It may also be prepared by decomposing the double sulphate of lead and oxide of methyle by sulphuretted hydrogen. The solution of the neutral sulphate of oxide of methyle in boiling water, if allowed to evaporate spontaneously, yields this compound very pure.

It is a colourless, syrupy liquid, very acid; which, in a dry atmosphere, forms a mass composed of white needles. When prepared from the salt of baryta, it is decomposed in vacuo, giving off sulphurous acid; it is more stable when made from the neutral sulphate. Heat accelerates its decomposition.

It mixes in all proportions with water, and is soluble in alcohol. In contact with bases, it forms double salts, in which the hydratic water of the acid is replaced by 1 eq. of metallic oxide. All these salts are soluble in water.

DOUBLE SALTS OF THE SULPHATE OF OXIDE OF METHYLE.

Syn. Sulphomethylates.—These double salts, when their solutions are boiled or evaporated, undergo decomposition, yielding products exactly analogous to those formed from the corresponding salts of ethyle.

When subjected to dry distillation, they yield, among other products, a large quantity of neutral sulphate of oxide of methyle.

The double salts of sulphate of oxide of methyle with *ammonia* and *oxide of ethyle* have not yet been formed.

Sulphate of Potash and Oxide of Methyle.—Formula, $\text{MeO}, \text{KO}, 2\text{SO}_3 + \text{aq.}$ (Kane.) This salt is obtained by precipitating the

double salt of baryta by carbonate of potash. It crystallizes in rhomboidal tables, which have the lustre of mother-of-pearl, and are deliquescent in a moist air. They differ from the corresponding salt of ethyle in containing water of crystallization.

When this salt is dissolved in a strong solution of ferrocyanide of potassium, there are obtained, by the evaporation of the mixture, two salts: first, a yellow salt, easily crystallizable, insoluble in alcohol, very similar in aspect to the ferrocyanide of potassium; and afterwards a white salt, which is soluble in alcohol. These salts were discovered by Gregory. They are double salts: the yellow salt is a compound of ferrocyanide of potassium with ferrocyanide of methyle; the white appears to contain cyanide of methyle, bisulphate and sulphate of potash, and oxide of methyle. Similar compounds are obtained by treating in the same way the corresponding salt of ethyle. (Gregory.) These compounds merit a more minute investigation.

Sulphate of Baryta and Oxide of Methyle.—Formula, $\text{MeO}, \text{BaO}, 2\text{SO}_3 + 2\text{aq.}$ (Dumas and Peligot.) To obtain it, equal weights of oil of vitriol and pyroxylic spirit are mixed, and heated to the boiling point. When cold, water is added, and the liquid is neutralized, first with carbonate of baryta, and finally with pure baryta. After removing the excess of baryta by a current of carbonic acid, the filtered liquid is gently evaporated. The double salt crystallizes in square tables, colourless and transparent, efflorescing in the air. In vacuo, they lose all their water of crystallization and become opaque. This salt is used for the preparation of the bisulphate of oxide of methyle; and, when mixed with soluble sulphates, it yields the other double salts of methyle.

Sulphate of Lead and Oxide of Methyle.—Formula, $\text{MeO}, \text{PbO}, 2\text{SO}_3 + \text{aq.}$ (Kane.) Prepared in the same way as the preceding salt. It is deliquescent. Kane has sometimes obtained it in the same form as the salt of baryta, and containing 2 at. of water of crystallization.

The *Phosphate of Oxide of Methyle* has not yet been obtained.

Nitrate of Oxide of Methyle.—Formula, MeO, NO_5 . (Dumas and Peligot.) The action of nitric acid on pyroxylic spirit is different from its action on alcohol. The latter is easily decomposed by it, yielding oxidized products, with nitrate of oxide of ethyle: the latter is only changed by it when boiled. A large excess of nitric acid converts it into formic and oxalic acids, without any nitrite or nitrate of oxide of methyle. The nitrite appears not to exist: the nitrate, on the contrary, is easily obtained.

For this purpose, 1 part of nitre is introduced into a retort with

a mixture of 2 parts of oil of vitriol and 1 part of pyroxylic spirit. The mass becomes very hot, and the new compound distils over without external heat. The receiver must be carefully cooled; and in it two liquids condense, of which the heavier is nitrate of oxide of methyle. It is mixed with a very volatile compound, perhaps formate of oxide of methyle, and has the odour of prussic acid. To purify it, it is rectified with an excess of chloride of calcium and oxide of lead. The last portions are perfectly pure.

It is a colourless liquid, having a faint ethereal smell. Its density is 1.182 at 72°; it boils at 151°; is inflammable, and burns with a yellow flame. Its vapour, heated above 248°, detonates with great violence; producing water, carbonic acid, and deutoxide of nitrogen. It is soluble in water, and miscible in all proportions with alcohol, ether, and pyroxylic spirit.

It is slowly decomposed by aqua ammoniæ or aqua potassæ; rapidly by an alcoholic solution of potash. The products are nitrate of potash and pyroxylic spirit.

Carbonate of Oxide of Methyle.—The neutral salt is not known. The double salts which it forms with the alkaline carbonates are obtained in the same way as the corresponding salts of ethyle.

Oxalate of Oxide of Methyle.—Formula, $\text{MeO}, \bar{\text{O}}$. (Dumas and Peligot.) To obtain it, equal parts of sulphuric acid, oxalic acid, and pyroxylic spirit are distilled; or 2 parts of sulphuric acid may be distilled with one part of binoxalate of potash and 1 part of pyroxylic spirit. The oxalate is obtained in the receiver, partly pure in the form of crystals, partly dissolved in pyroxylic spirit. The whole is allowed to evaporate in a warm place; the crystals are dried by pressure in bibulous paper, and redistilled with oxide of lead to remove any free oxalic acid.

This compound forms a white, solid, transparent mass, composed of rhomboidal tables. It melts at 124°, and boils at about 322°. It is easily dissolved by water, producing hydrated oxalic acid and pyroxylic spirit. It is soluble in alcohol and pyroxylic spirit, more so with the aid of heat; and these solutions, saturated when hot, deposit large transparent crystals on cooling.

Dry ammonia converts it into oxamethylane; aqua ammoniæ converts it into oxamide and pyroxylic spirit. The reaction is the same as with the corresponding compound of ethyle.

The *Binoxalate of Oxide of Methyle* is not known.

Oxamate of Oxide of Methyle. *Syn. Oxamethylane.*—Formula, $\text{C}_6\text{H}_5\text{NO}_6 = \text{MeO} + \text{O}, \text{C}_2\text{O}_2$. Ad. (Dumas and Peligot.) When a current of dry ammonia is passed over melted oxalate of methyle, the

latter is gradually converted into a white solid mass. Alcohol dissolves it, and by evaporation deposits the oxamethylene in cubical crystals with the lustre of mother-of-pearl.

Bisulphocarbonate of Oxide of Methylene.—Formula, $2\text{CS}_2, \text{MeO}$. This compound is formed in the same way as the corresponding compound of ethyle. According to Dumas and Peligot, the double sulphocarbonate of oxide of methyle and potash may be obtained by adding hydrate of potash to a solution of the bisulphuret of carbon in pyroxylic spirit.

Allophanate of Oxide of Methylene.—When hydrated cyanic acid, in vapour, is passed into pyroxylic spirit, there is formed this compound, quite analogous to the corresponding salt of ethyle. Its formula is $\text{MeO} + \text{C}_4\text{N}_2\text{H}_3\text{O}_5$.

Benzoate of Oxide of Methylene.—Formula, $\text{BzO}, \text{MeO} = \text{C}_{14}\text{H}_5\text{O}_3, \text{C}_2\text{H}_3\text{O}$. (Dumas and Peligot.) This compound is best obtained by distilling a mixture of dry benzoate of lime or of soda with neutral sulphate of methyle, or 2 parts of benzoic acid with 1 part of sulphuric acid and 1 part of pyroxylic spirit. It is an oily, colourless liquid, having a balsamic odour, not unlike that of the oil of bitter almonds. It is heavier than water, and boils at 227° : insoluble in water; soluble in alcohol, pyroxylic spirit, and ether. The density of its vapour is found to be 4.7506, representing 4 volumes; the calculated density is $\frac{18.996}{4} = 4.749$.

Acetate of Oxide of Methylene.—Formula, $\text{MeO}, \text{AcO}_3 = \text{C}_2\text{H}_3\text{O}, \text{C}_4\text{H}_3\text{O}_3$. (Dumas and Peligot.) This compound is prepared by distilling 2 parts of pyroxylic spirit with 1 of hydrated acetic acid and 1 of oil of vitriol. An acetate may be substituted for the acetic acid. The product is put in contact with fragments of chloride of calcium, which, combining with the free pyroxylic spirit, separates the acetate as a light liquid. According to Berzelius, it is contained in abundance in the raw pyroxylic spirit. Reichenbach, having extracted it therefrom, although not in a state of purity, considered it as a peculiar combination, to which he gave the name of Mesite. Berzelius has given a process by which it may be extracted from the raw liquor. The presence of a large proportion of this substance is the cause of the fluidity of wood tar.

It is a colourless liquid, having a pleasant smell, like that of pyroxylic spirit, and a burning taste. Its sp. gr. is 0.919 at 70° . It boils at 136° . (Dumas and Peligot.) The mesite of Reichenbach has the sp. gr. 0.805, and boils at 144° . The acetate of methyle dissolves $\frac{1}{2}$ part of water, and is itself dissolved by 2 parts of water. It mixes in all proportions with alcohol and pyroxylic spirit, and is sepa-

rated from these solutions by chloride of calcium and hydrate of potash. Chlorine decomposes it, producing hydrochloric acid. When mixed with oil of vitriol, it becomes very hot, and is decomposed. Hydrate of lime converts it into acetate of lime and pyroxylic spirit.

It dissolves many salts, vegetable acids, oils, both fixed and volatile, and several resins. It contains the same elements, in the same proportions, but differently grouped, as the formiate of oxide of ethyle; for $C_2H_3O, C_4H_3O_3 = C_4H_5O, C_2HO_3 = C_6H_6O_4$.

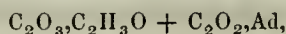
Mucate of Oxide of Methyle.—Formula, $2MeO + \bar{Mu}$. (Malaguti.) Prepared exactly as the mucate of ethyle, using pyroxylic spirit instead of alcohol. It is a white crystalline substance, decomposed by a heat of 326° . It is soluble in alcohol, from which it crystallizes in six-sided rhombic prisms. It is very soluble in water. The crystals from its aqueous solution have a density of 1.53, whereas those formed in alcohol have a density only of 1.48.

COMPOUNDS OF METHYLE OF UNCERTAIN CONSTITUTION.

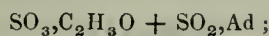
Oxychlorocarbonate of Oxide of Methyle.—Formula, $C_4H_3ClO_4$. (Dumas and Peligot.) The preparation and properties of this body are similar to those of the corresponding compound of ethyle. Dumas and Peligot express its constitution by the formula $C_2 \left\{ \begin{smallmatrix} O_3 \\ Cl \end{smallmatrix} \right\} + C_2H_3O$. According to this, it would be composed of oxide of methyle united to a peculiar acid.

Urethylane.—The preceding compound, in contact with ammonia, appears to undergo a change analogous to that described under the corresponding compound of ethyle. Dumas and Peligot have shewn that there are formed sal-ammoniac and a deliquescent crystallizable mass, to which they have given the name Urethylane, corresponding to urethane, formerly described. It is, no doubt, the carbamate of oxide of methyle: $C_4NH_5O_4 = MeO + CO_2, CONH_2$.

Sulphamethylane.—When a current of dry ammonia is passed through neutral sulphate of methyle, heat is developed, and a new substance is formed, to which Dumas and Peligot have given the name of Sulphamethylane. It may also be obtained by using aqua ammoniæ. In this case a liquid is obtained, which, if evaporated in vacuo, deposits large crystals of the new compound. It is very deliquescent. Its empirical formula is $C_2H_5NS_2O_6$. It is a compound analogous to oxamethylane: if the latter be represented by



sulphamethyle will be represented by

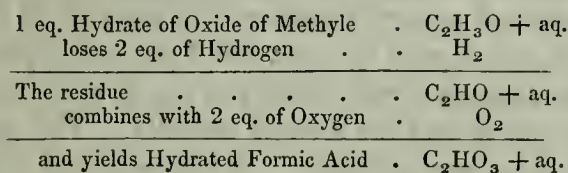


that is, a compound of sulphate of methyle with sulphamide, or of oxide of methyle with sulphamidic acid, $\text{SO}_3, \text{AdSO}_2$, as oxamethyle is of oxide of methyle with oxamidic acid.

PRODUCTS OF THE DECOMPOSITION OF METHYLE AND OF THE SUBSTANCES DERIVED FROM IT.

Hitherto we have but few exact researches on the transformations of methyle and its compounds. With reference to the existence of an acid corresponding to isethionic acid, Dumas and Peligot have found, that, when anhydrous sulphuric acid is mixed with pyroxylic acid, the mixture being carefully cooled, an acid is obtained, which forms with baryta a soluble and crystallizable salt, having the same composition as the double sulphate of methyle and baryta, but differing from that salt in its properties.

When pyroxylic spirit is oxidized by means of the powder of platinum and air, as described under alcohol, it undergoes a slow combustion, similar to that of alcohol in the same circumstances. The oxygen of the air, condensed by the platinum, combines with the hydrogen of the spirit, and replaces that which is removed, equivalent for equivalent. The final product of this reaction is a very acid liquid, which is found to be pure formic acid.

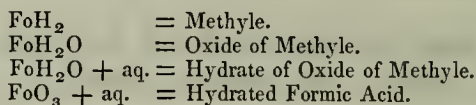


It is obvious that there is the same relation between pyroxylic spirit and formic acid as between alcohol and acetic acid. We have, therefore, good reason to believe that formic acid is the oxide of a radical, C_2H , analogous to acetylene, which has been called *Formyle*. By formyle, then, is to be understood a hypothetical radical whose formula is C_2H .

We shall describe the changes produced on methyle and its compounds by chlorine, &c., in treating of the compounds of formyle with chlorine, bromine, &c.

FORMYLE.

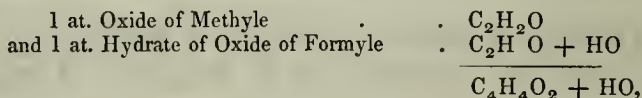
Formula, C_2H . Symbol, Fo. As ethyle may be considered as the hyduret of acetylene, AcH_2 , so methyle may be viewed as the hyduret of formyle, FoH_2 . We shall then have



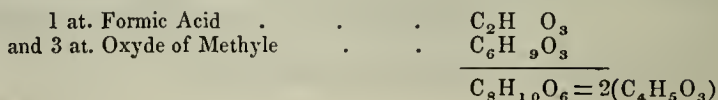
The compound corresponding to aldehyde has not yet been discovered. Its formula would be $FoO + aq. = C_2HO + aq.$ In like manner, the compound analogous to the aldehydic or acetylous acid is not yet known. The following table contains the principal compounds of the series of formyle:—

C_2HO	Oxide of Formyle, unknown.
$C_2HO + aq.$	Hydrate of the above, contained in Formomethylal.
C_2HO_3	Anhydrous Formic Acid.
$C_2HO_3 + aq.$	Hydrated Formic Acid.
C_2HCl_3	Perchloride of Formyle.
C_2HBr_3	Perbromide of Formyle.
C_2HI_3	Periodide of Formyle.

Gregory first observed that by distilling a mixture of pyroxylic spirit, hyperoxide of manganese, and sulphuric acid, a peculiar liquid is obtained. Kane subsequently examined this substance with care, and described it under the name of *Formomethylal*. He prepared it by distilling 2 parts of pyroxylic spirit with 3 parts of oil of vitriol, previously mixed with 3 parts of water, and 2 parts of hyperoxide of manganese. The reaction is very violent; so that it is necessary to employ a water-bath, and to cool the receiver carefully. The product is very impure, containing several liquids. It begins to boil at 100° , but the boiling point gradually rises to 177° . The liquid which passes first reduces the nitrate of silver with the aid of ammonia and a gentle heat, as aldehyde does. A liquid then comes, which boils steadily at 100° . This is Kane's formomethylal. Several analyses led to the formula $C_4H_5O_3$; according to which it might be either a compound of



or a compound of



In support of the latter view,—namely, that it is a tribasic formiate of methyle,—Kane adduced the fact, that, when treated with an alcoholic solution of potash, it yields formiate of potash and pyroxylic spirit. But Malaguti shewed that the quantity of formic acid produced was never more than half of that indicated by the formula; and in the course of his researches he succeeded in proving that it is a mixture of neutral formiate of methyle and another liquid, which he has named *Methylal*.

Methylal.—Formula, $C_6H_8O_4$. (Malaguti.) To obtain it, the product of the distillation above described is mixed with water, and distilled with potash ley. The product is saturated with solid caustic potash, which separates an ethereal liquid. This is mixed with water, and again rectified with potash, so as to purify it entirely from formiate of oxide of methyle.

Methylal is an ethereal liquid of an agreeable odour. It is dissolved by three parts of water, from which it is separated by caustic potash or chloride of calcium. It is miscible in all proportions with pyroxylic spirit, alcohol, and ether. It boils at 108° , and has the sp. gr. 0.855. It is inflammable, and burns with a luminous flame. Oxidizing agents convert it into formic acid. Chlorine destroys it; producing, among other products, sesquichloride of carbon. (Malaguti.) According to the formula, $C_6H_8O_4$, representing 4 vol. of vapour, this substance may be regarded as a compound of 1 at. hydrate of oxide of formyle, and 2 at. oxide of methyle $= C_2HO, HO + 2C_2H_3O$.

Regnault has started a very ingenious conjecture relative to the formation of this compound. He supposes that 3 at. of oxide of methyle, formed by the action of the sulphuric acid on the pyroxylic spirit, group themselves into one $= C_6H_9O_3$; this, again, exposed to the oxidizing agency of the hyperoxide of manganese, loses 1 at. hydrogen, which is replaced by 1 at. oxygen, thus yielding the compound $C_6H_8O_4$.

The corresponding compound in the series of ethyle is acetal, $C_8H_9O_3$, which we have considered as a compound of 1 at. hydrated oxide of acetylene (aldehyde), and 1 at. oxide of ethyle $= AcO, HO + AeO$. Regnault explains its formation in a manner analogous to that proposed by him for methylal, supposing 2 at. of oxide of ethyle to be grouped into 1 $= C_8H_{10}O_2$; and that this, losing 1 at. of hydrogen, and gaining 1 at. oxygen, yields acetal. These different views are essentially the same.

FORMIC ACID.

Formula, $C_2HO_3 + aq.$ The production of this acid by the oxidation of the hydrated oxide of methyle (pyroxylic spirit), has been already described. It was first discovered in the red ant (*Formica rufa*), whence its name; Gehlen first recognized it as a peculiar acid. Doebereiner was the first who prepared it artificially by distilling tartaric acid with sulphuric acid and hyperoxide of manganese. All vegetable substances produce formic acid, carbonic acid, and sometimes acetic acid, when distilled with nitric acid, periodic acid, iodic acid, hypermanganic acid, a mixture of chromic and sulphuric acids, or of sulphuric acid with hyperoxide of manganese, or bichromate of potash.

Formic acid is further produced by the action of alkalies on chloral, and by the decomposition of metallic cyanides or hydrocyanic acid by strong acids or alkalies. It is likewise a product of the dry distillation of effloresced (monohydrated) oxalic acid, and of the distillation of organic matters with fused potash at a high temperature.

To obtain the hydrated formic acid, $C_2HO_3 + aq.$, dry formiate of lead in fine powder is introduced into a long glass tube; one end of which is connected with a receiver, the other with an apparatus from which sulphuretted hydrogen gas is disengaged. When the formiate of lead is entirely decomposed, which is known by its becoming black throughout, the formic acid is driven into the receiver by a very gentle heat. If the heat be too strong, decompositions of a different kind occur, producing sulphuretted compounds not yet examined. To purify the acid obtained from any excess of sulphuretted hydrogen, it is boiled for a very short time.

The hydrated formic acid is a limpid and colourless liquid, which fumes slightly, and attracts the moisture of the air. It has a penetrating odour, and below 32° it crystallizes in brilliant scales. It boils at 212° , and has the sp. gr. 1.2353. The vapour of the boiling acid is inflammable, and burns with a blue flame.

It is miscible with water in all proportions. With a quantity of water equal to that which it already contains, (20 p. c.,) it forms a second hydrate, $C_2HO_3 + 2 aq.$, which has the same properties as the first, except that it boils at 223° , and does not solidify at 5° , and that its sp. gr. is 1.1104 at 60° . This second hydrate is easily obtained by distilling, in a bath of chloride of calcium, 18 parts of dry formiate of lead, 6 of oil of vitriol, and 1 of water.

Both these hydrates are exceedingly corrosive; a drop of either placed on a tender part of the skin produces an actual burn, which

suppurates, causing intolerable pain, and is very difficult to heal. A more diluted acid, but equally pure, is obtained by distilling 10 parts of formiate of lime, 8 parts of oil of vitriol, and 4 of water. These propositions yield 9 parts of formic acid, sp. gr. 1.075.

In order to obtain a diluted and impure acid, from which the salts of formic acid may be obtained, bruised ants may be distilled with water; or, according to Emmet, equal volumes of sulphuric acid, water, and wheat, rye, or starch, may be heated till the mixture blackens. It is then allowed to cool; and, after adding water equal to one-third of the whole bulk of the mixture, distilled in a copper alembic. The acid liquor obtained is turbid from the presence of oily matter, and contains much sulphurous acid. Phosphoric acid or chloride of tin may be substituted for the sulphuric acid in this operation, which proves that the oxygen of the sulphuric acid is not concerned in the production of the formic acid; but the reaction by which it is formed is not understood.

By distilling 1 part of starch with 4 of hyperoxide of manganese in fine powder, 4 of oil of vitriol, and 4 of water, we may obtain an impure formic acid, sp. gr. 1.025: 100 parts of such acid neutralize 10.6 parts of dry carbonate of soda. When the mixture is heated there is a great disengagement of carbonic acid, so that it froths up very much. Hence it is better to introduce into the alembic first the oxide of manganese, the starch, and the water; to heat the mixture to 104° , and then to add the acid by degrees. When all the acid has been added, and the frothing is over, heat is applied, and $4\frac{1}{2}$ parts of liquid are distilled off.

The best proportions for preparing formic acid on a smaller scale in glass vessels are 10 parts of starch, 37 of oxide of manganese, 30 of oil of vitriol, and 30 of water. The retort ought to have a capacity equal to 10 times the bulk of the mixture. These materials yield 3.35 parts of an acid, of which 100 parts neutralize 15 of dry carbonate of soda.

Formic acid is easily recognized by the reactions which it exhibits with sulphuric acid, and with the oxides of mercury and silver. An excess of sulphuric acid decomposes it without blackening, with a brisk effervescence; producing pure carbonic oxide gas, and water, which combines with the sulphuric acid. $C_2HO_3 + HO,SO_3 = SO_3,2HO + 2CO$.

When formic acid is heated with the oxide of mercury or of silver, it is completely destroyed; carbonic acid gas is disengaged, water is produced, and the metal is reduced, no trace of it remaining in the liquid. If the formic acid contain acetic acid, the latter is found in the liquid, in combination with the oxide of mercury or of silver.

Corrosive sublimate, heated with formic acid, is reduced to calomel, while hydrochloric and carbonic acids are disengaged.

The soluble salts of mercury and silver are reduced by formic acid just as the oxides are.

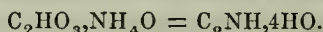
Peroxides are reduced, when heated with formic acid, to protoxides, which combine with the formic acid, carbonic acid being disengaged.

FORMIATES.

Formic acid has a stronger affinity for bases than acetic acid. Its salts may be obtained by saturating the acid with an oxide or a carbonate. They are all soluble in water. The alkaline formiates, when heated, blacken, give off inflammable gases, and leave a residue of carbonate. The other formiates, in the same circumstances, give off carbonic acid, carburets of hydrogen, and water; and leave a residue of carbon, and of oxide or reduced metal.

When a formiate in excess is boiled with the solutions of mercury, silver, platinum, and gold, the metals are completely reduced, with disengagement of carbonic acid gas. Sulphuric acid acts on the formiates as it does on the free acid. The salts of sesquioxide of iron are coloured of a deep yellowish red by the formiates.

Formiate of Ammonia.—Formula, $\text{FoO}_3, \text{NH}_3, \text{HO} = \text{FoO}_3, \text{AdH}_2\text{O}$. The solution of this salt becomes acid when evaporated, ammonia being disengaged. It crystallizes in four-sided rectangular prisms, terminated by four faces. It is deliquescent, has a cool and pungent taste, melts at 248° , and is volatilized without residue at a higher temperature. It contains the elements of 1 eq. hydrocyanic acid and 4 eq. water.



It is actually transformed into these products when its vapour is passed through a red-hot tube. (Doebereiner; Pelouze.)

Formiate of Melamine.—This salt crystallizes in shining scales, which lose a part of their acid when exposed to the air, especially if heated to 212° .

Formiate of Oxide of Ethyle. Syn. Formic Ether.—Formula, FoO_3, AeO . To prepare it, 7 parts of dry formiate of soda are introduced into a retort connected with a refrigeratory, along with a mixture of 10 parts of oil of vitriol, and 6 of alcohol at 90 p. c. By the heat spontaneously developed, the greater part of the formic ether distils without the application of external heat. It is purified from acid by agitation with milk of lime, and from water by chloride of calcium, which is added as long as it is moistened.

The formiate of ethyle is a limpid liquid, of a penetrating aromatic smell, and has the sp. gr. 0.912. It boils at 128° ; its taste is cooling and spicy. It is soluble in 10 parts of water, and miscible in all proportions with alcohol, ether, pyroxylic spirit, and several fixed and volatile oils. It quickly becomes acid when exposed to the air.

Formiate of Oxide of Methyle.—Formula, FoO_3, MeO . Prepared like the preceding compound. A very mobile liquid, lighter than water; boiling about 98° . Its odour resembles that of acetic ether.

Formiate of Potash.—A deliquescent salt, which can hardly be crystallized.

Formiate of Soda.—Formula, $\text{FoO}_3, \text{NaO} + 2 \text{ aq}$. Prepared by decomposing formiate of lead with carbonate of soda. It crystallizes in rhombic prisms or tables, of a bitter saline taste. When heated, they melt in their water of crystallization; and at a higher temperature they are decomposed. It is deliquescent in a moist air; insoluble in alcohol. According to Goebel, this salt, when heated with a great many metallic oxides, in the dry state, reduces them. He recommends it as a powerful reducing flux for blowpipe experiments. Doebereiner has proposed to employ its solution to separate silver, mercury, platinum, and palladium from iron, copper, manganese, &c. When solutions containing these metals are boiled with formiate of soda, the former are precipitated in the metallic state; the latter are not affected.

Formiate of Baryta.—Formula, FoO_3, BaO . This salt crystallizes easily in transparent prisms of a high lustre, permanent in the air. It is very bitter to the taste, soluble in 4 parts of water, insoluble in alcohol. (Arfvedson.)

Formiate of Strontia.—Formula, $\text{FoO}_3, \text{SrO} + 4 \text{ aq}$. Six-sided prisms, brilliant and transparent, permanent in the air. Heat expels the water of crystallization.

Formiate of Lime.—Formula, FoO_3, CaO . This salt is easily obtained pure by supersaturating with milk of lime the impure formic acid prepared by the processes above described from starch or other organic matters. The sulphurous acid which it contains is precipitated as insoluble sulphite of lime, and the excess of lime is removed by a current of carbonic acid. As the salt is hardly more soluble in hot than in cold water, the best way to crystallize it is to evaporate the solution by a gentle heat. During the evaporation it deposits snow-white needles. (Goebel.) It yields very pure formic acid, when distilled with sulphuric acid, more or less diluted.

Formiate of Magnesia.—Formula, FoO_3, MgO . Fine brilliant needles, permanent in the air, soluble in 13 parts of water. (Goebel.)

Formiate of Alumina.—Formula, $3\text{FoO}_3, \text{Al}_2\text{O}_3$. This salt forms, when evaporated, a gummy mass. Its solution is permanent when boiled; if sulphate of potash or alum be added, it becomes turbid when heated, but clears up again on cooling; a property which this salt has in common with the acetate of alumina.

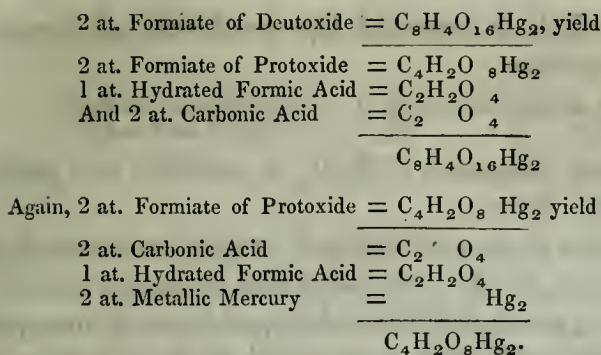
The *Formiates of Manganese, Protoxide of Iron, Zinc, Cadmium, Nickel, and Cobalt*, are very soluble and crystallizable.

The *Formiate of Cerium* has been described as a white crystalline powder, very sparingly soluble; and it has been proposed to make use of this property for purifying oxide of cerium from other oxides: but the recent discovery of a new metal, *Lantanum*, in the oxide hitherto considered as oxide of cerium, renders it necessary that new researches should be made to ascertain the properties of the salts, both of lantanum and of cerium, when separated from that metal.

Formiate of Copper.—This salt crystallizes in large rhomboidal prisms, very regular, transparent, of a light blue colour. It effloresces when heated.

Formiate of Lead.—Formula, FoO_3, PbO . When formic acid is added to a saturated solution of acetate of lead, it causes, after a short time, a deposition of brilliant needles of this salt. It is easily obtained from the impure formic acid above mentioned by boiling it with carbonate of lead; the filtered solution deposits, on cooling, crystals of the formiate, which are easily purified by washing with cold water and a second crystallization. This salt requires 36 to 40 parts of cold water for solution, but is much more soluble in hot water. Its sparing solubility affords an easy method of purifying formic acid from acetic acid, the acetate of lead being very soluble. A perfect separation of these two salts may be made by alcohol, in which the formiate of lead is quite insoluble. This salt is used for preparing formic acid, strong or diluted; and also formiate of soda, as above described.

Formiates of Protoxide and Deutoxide of Mercury.—Formula, HgO, FoO_3 , and $\text{HgO}_2, 2\text{FoO}_3$. Finely powdered peroxide of mercury dissolves in formic acid at the ordinary temperature, forming a syrupy liquid, which by spontaneous evaporation yields a solid crystalline mass. The slightest heat decomposes this salt; carbonic acid is disengaged, formic acid set free, and formiate of protoxide is generated. This latter salt, when a solution of the former is gently heated, is deposited in brilliant silvery scales, which must be dried by pressure in bibulous paper. When heated, either in the dry state or in solution, this salt is decomposed, with a slight explosion in the former case, and effervescence in the latter; carbonic acid and formic acid being set free, and metallic mercury deposited. The following schemes explain these decompositions:—



Formiate of Silver.—Formula, AgH, FoO_3 . Prepared by mixing nitrate of silver with an alkaline formiate. It is deposited in shining scales, which are sparingly soluble, and are resolved by heat, like the preceding salt, into carbonic acid, formic acid, and metallic silver.

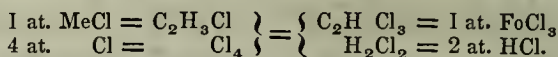
COMPOUNDS OF FORMYLE WITH CHLORINE, BROMINE, AND IODINE.

Chlorine and the hypochlorites act on the chloride, oxide, and hydrated oxide of methyle, producing a series of chlorides of formyle. As formic acid may be obtained from substances which do not contain formyle ready formed, so the chlorides of this radical may be obtained from substances which do not contain it. Thus *perchloride of formyle* is a product of the decomposition of chloral by alkalis; and the same compound is produced by distilling alcohol or acetone with hypochlorites. The *perbromide of formyle* is obtained in the same way from bromal; and the *periodide of formyle* by the action of iodine and potash on alcohol.

When chloride of methyle, $\text{C}_2\text{H}_3\text{Cl}$, is exposed to the rays of the sun in contact with chlorine, three distinct compounds are formed, which have been lately examined by Regnault. (Ann. de Chimie, vol. lxxi. p. 353.) That produced by the first reaction is $\text{C}_2\text{H}_2\text{Cl}_2$. It is a colourless liquid, boiling at 87° . The density of its vapour is 2.94. It is produced from the chloride of methyle by the loss of 2 at. hydrogen, which are replaced by 2 at. chlorine. Were the chlorine in this compound replaced by its eq. of oxygen, we should have a hydrated oxide of formyle corresponding to aldehyde, the formula of which would be $\text{C}_2\text{H}_2\text{O}_2 = \text{C}_2\text{HO, HO}$. It would be isomeric or rather polymeric with hydrated acetic acid $= \text{C}_4\text{H}_4\text{O}_4$, and with the formiate of methyle $= \text{C}_2\text{H}_3\text{O, C}_2\text{HO}_3$.

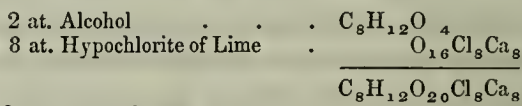
When this chloride is further acted on by chlorine, it is changed into perchloride of formyle, C_2HCl_3 , while hydrochloric acid is formed.

Chloride of methyle is converted into perchloride of formyle by the aid of 4 at. of chlorine.

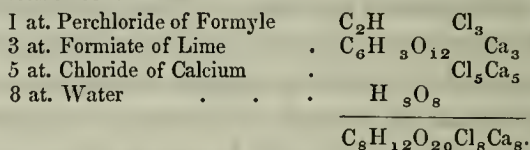


The intermediate compound, $\text{C}_2\text{H}_2\text{Cl}_2$, is converted into perchloride of formyle by 2 at. chlorine.

The production of the perchloride of formyle from alcohol, pyroxylic spirit, and acetone, is the result of a very complex reaction. When either of these liquids is distilled with hypochlorite of lime, perchloride of formyle distils over, while a compound of chloride of calcium and carbonate of lime is deposited in brilliant crystalline grains. The hypochlorite must have an alkaline reaction; if supersaturated with chlorine, the perchloride of formyle is not produced. No gas is disengaged, and in particular no carbonic acid is set free. When alcohol is employed, it is probable that chloral is first formed, and that the perchloride of formyle is formed by the decomposition of that substance. As the perchloride contains only one-fourth of the carbon contained in the alcohol employed to produce it, the following formulæ probably give a correct explanation of the reaction:—



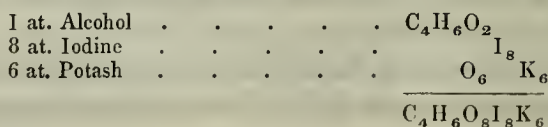
contain the elements of



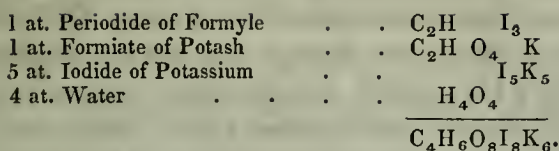
But 3 at. of formiate of lime, in contact with 3 at. of hypochlorite of lime and caustic lime in excess, are converted into 6 at. of carbonate of lime.

It is unnecessary to explain in detail the production of perchloride of formyle from oxide of methyle, since 4 at. of this substance contain the same elements, and in the same proportions, as 2 at. of alcohol. In like manner, as acetone may be viewed as a compound of 1 at. oxide of acetylene, $\text{C}_4\text{H}_3\text{O}$, and 1 at. oxide of methyle, $\text{C}_2\text{H}_3\text{O} = \text{C}_6\text{H}_6\text{O}_2$, the production of perchloride of formyle from it may easily be understood.

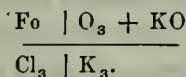
The periodide of formyle is produced by the reaction of 1 at. alcohol with 8 at. iodine, and 6 at. potash; yielding 1 at. periodide of formyle, 1 at. formiate of potash, 5 at. iodide of potassium, and 4 at. water.



are equivalent to



The compounds of iodine, bromine, and chlorine with formyle are all decomposed, although with difficulty, by the alkalis, yielding alkaline formiates and metallic iodides, &c. For example, 1 at. perchloride of formyle gives, with 4 at. potash, 1 at. formiate of potash, and 3 at. chloride of potassium.



Protochloride of Formyle.—Formula, $\text{C}_2\text{HCl} = \text{FoCl}$. By the action of chlorine on chloride of acetylene, Regnault obtained a compound, $\text{C}_4\text{H}_2\text{Cl}_2$, which, if halved, would represent the protochloride of formyle. (See Chloride of Acetylene.)

Bichloride of Formyle.—Formula, $\text{C}_2\text{HCl}_2 = \text{FoCl}_2$. In speaking of the action of chlorine on the compounds of ethylene and of acetylene, we have already mentioned a substance obtained by Regnault as a product of the action of chlorine on chloride of ethylene. This substance may be $\text{C}_4\text{H}_2\text{Cl}_4$, or bichloride of formyle, C_2HCl_2 .

Perchloride of Formyle. *Syn. Chloroform.*—Formula, $\text{C}_2\text{HCl}_3 = \text{FoCl}_3$. (Dumas.) It is obtained either by distilling chloral with milk of lime, or, as above mentioned, by distilling alcohol, pyroxylic spirit, or acetone, with hypochlorite of lime. The product is mixed with water, which separates the perchloride. It is rectified in the water-bath, dried by digestion with chloride of calcium, and finally distilled with oil of vitriol.

It is a colourless oily liquid, having an agreeable ethereal smell and a sweet taste. Its sp. gr. is 1.480, and it boils at about 140°. An alcoholic solution of potash converts it into formiate of potash. (Dumas.) The density of its vapour is 4.2. Calculation gives $\frac{16.465}{4} = 4.116$, representing 4 volumes. It is not altered by distillation with potassium, potash, sulphuric acid, and other acids. When its vapour is passed through a red-hot tube, it is decomposed into carbon, hydrochloric acid, and a crystalline body, which appears in long white needles.

When exposed to the rays of the sun in contact with chlorine, it yields a chloride of carbon, C_2Cl_4 , which boils at 173°, and the vapour of which has the density 5.30. (Regnault.) Calculation gives the same number, $\frac{21.209}{4} = 5.30$, representing 4 volumes. This

compound may be considered as formic acid in which both the hydrogen and oxygen have been replaced by chlorine, $C_2Cl + Cl_3$. In this point of view it has a great analogy with the sesquichloride of carbon, $C_4Cl_6 = C_4Cl_3 + Cl_3$; which has the same relation to acetic acid, as the chloride of carbon now described has to formic acid. When the chloride, C_2Cl_4 , is made to pass through a red-hot tube, it is resolved, according to Regnault, into two new chlorides of carbon, represented by the formulæ C, Cl_3 and C, Cl .

Hydrochlorate of Chloride of Formyle.—Formula, $2C_2HCl, HCl$. When chlorine acts on the hydrochlorate of chloride of acetylene, this compound is formed along with other products. (Regnault.)

Perbromide of Formyle. Syn. Bromoform.—Formula, $C_2HBr_3 = FoBr_3$. (Dumas.) It is prepared exactly as the perchloride, bromine being substituted for chlorine. It resembles the perchloride, but is heavier, having in the liquid form the sp. gr. 2.10; and is more easily decomposed by alkalis.

Periodide of Formyle. Syn. Iodoform.—Formula, $C_2HI_3 = FoI_3$. (Dumas; Mitscherlich.) Discovered by Serullas, who described it first as a compound of iodine with carburetted hydrogen, and subsequently as iodide of carbon. Mitscherlich also described it as an iodide of carbon; which for some time led to erroneous views of the nature of chloroform, the corresponding compound of chlorine. Dumas first ascertained its true composition. To obtain it, an alcoholic solution of potash is added to an alcoholic solution of iodine, till the latter is decolorized, avoiding all excess of potash. The alcohol is then expelled by gentle evaporation, when the iodide of formyle is deposited in crystals, which are purified from iodide of potassium by washing with cold water.

It crystallizes in pale yellow shining scales, having a slight but disagreeable odour, resembling that of saffron, and adhering strongly to the hands, or to substances brought in contact with it. It is insoluble in water; very soluble in alcohol, ether, and pyroxylic spirit. It sublimes at 212° ; and at 248° it is decomposed, yielding iodine, carbon, and hydriodic acid. It is rapidly decomposed by an alcoholic solution of potash. Chlorine, with the aid of heat, converts it into perchloride of formyle and chloride of iodine. When distilled with chloride of phosphorus or corrosive sublimate, it yields a dark red liquid, sp. gr. 1.96, which contains chlorine, iodine, and formyle.

Sulphuret of Formyle. Syn. Sulphoform.—Formula, FoS_3 ? (Boucharlat.) When 1 part of periodide of formyle is distilled with 3 parts of sulphuret of mercury, there is formed a yellow oily liquid, heavier than oil of vitriol, and insoluble in water. It is converted by

an alcoholic solution of potash into sulphuret of potassium and formiate of potash.

ACTION OF CHLORINE ON THE COMPOUNDS OF METHYLE.

Chlorine and Oxide of Methylene.—Chlorine decomposes the gaseous oxide of methyle with disengagement of hydrochloric acid; and converts it, according to Regnault, into an oily liquid, the formula of which is C_2H_2ClO . This liquid is very mobile, has a suffocating odour, causing a flow of tears, and resembling that of phosgene gas. In a moist air it gives off acid fumes. It may be distilled without change. Its sp. gr. is 1.315 at 68° : it boils at 221° . The density of its vapour was found = 4.047, representing 2 volumes. Calculation gives $\frac{7.944}{2} = 3.972$. Regnault calls this compound *Monochloruretted Methylic Ether*.

By the further action of chlorine on this compound, Regnault obtained a liquid of a less powerful odour, sp. gr. 1.606 at 68° , boiling at 266° . Its formula is C_2HCl_2O . The density of its vapour was found = 6.367, representing 2 volumes. By calculation it is $\frac{12.697}{2} = 6.348$. This compound, which Regnault calls *Bichloruretted Methylic Ether*, may be viewed as an oxychloride of formyle, corresponding to formic acid in which 2 eq. oxygen are replaced by 2 eq. chlorine, $C_2H\left\{\begin{matrix} Cl_2 \\ O \end{matrix}\right\}$.

Finally, if the action of chlorine is prolonged, this substance loses all its hydrogen, yielding a very volatile body, C_2Cl_3O , called by Regnault *Perchloruretted Methylic Ether*. Its odour is strong and penetrating. Its sp. gr. is 1.594, and it boils at about 212° . The density of its vapour is 4.670, representing 4 volumes; not 2, like the preceding compounds: by calculation it is $= \frac{17.430}{4} = 4.36$.

The preparation of these compounds is dangerous, as violent explosions are likely to occur, unless the precautions recommended by Regnault in his memoir (*Ann. de Chimie*, vol. lxxi. p. 353) are observed.

Chlorine and Pyroxylic Spirit.—When chlorine gas is passed through pyroxylic spirit, it is absorbed with evolution of heat and light; and the action is so violent as to cause dangerous explosions, unless the apparatus be screened from light. Towards the end of the operation a gentle heat is required. Two liquids are thus obtained: one aqueous, containing much hydrochloric acid; the other, a heavy oily liquid, which has a pungent taste, and is decomposed by alkalis into formic acid and a new oily liquid. Kane has analyzed the first

liquid; but, as the products of its decomposition are not exactly determined, we cannot assign its true formula, nor can we at present explain its formation.

Chlorine and Chloride of Methylene.—We have already mentioned, in treating of the chlorides of formyle, the conversion of chloride of methyle into chloride of formyle by the action of chlorine. We have also mentioned that when the perchloride of formyle is further acted on by chlorine, with the help of the sun's rays and a gentle heat, chloride of carbon, C_2Cl_4 , is obtained. The products of the action of chlorine on chloride of methyle are therefore the substance $C_2H_2Cl_2$, perchloride of formyle C_2HCl_3 , and the chloride of carbon C_2Cl_4 . These compounds are all derived from the chloride of methyle, C_2H_3Cl , by the gradual replacement of its hydrogen by chlorine.

Chlorine and Sulphuret of Methylene.—According to Regnault, the sulphuret of methyle, C_2H_3S , is easily decomposed by chlorine, which converts it into a yellow oily liquid, of a most offensive smell. When the action is complete, the formula of the compound, by an approximative analysis, appears to be C_2Cl_3S ; the hydrogen being entirely replaced by chlorine: but, before reaching this point, the reaction seems to yield successively the compounds C_2H_2ClS and C_2HCl_2S .

Chlorine and Oxalate of Methylene.—When chlorine is made to act on the oxalate of oxide of methyle, several volatile substances are formed: one of which dissolves in water, with disengagement of carbonic acid; and another, when mixed with water, produces oxalic acid, with disengagement of carbonic oxide. Malaguti attributes this last reaction to the decomposition of a substance containing the elements of oxalic acid, chloride of carbon, and water $C_2O_3 + C_2Cl_2 + HO$. The chloride of carbon, in contact with water, produces hydrochloric acid and carbonic oxide. If this compound be represented by the formula $C_2O_3 + C_2H \left\{ \begin{smallmatrix} Cl_2 \\ O \end{smallmatrix} \right\}$ it will be the oxalate of the oxychloride of formyle; and its formation is easily explained. The chlorine, acting on the oxide of methyle, as formerly explained, produces oxychloride of formyle, which unites with the oxalic acid.

Chlorine and Benzoate of Methylene.—Chlorine acts on benzoate of oxide of methyle; producing, among other products, hydrochloric acid, chloride of benzoyle, and a compound analogous to the preceding, namely, benzoate of oxychloride of formyle, $BzO, C_2H \left\{ \begin{smallmatrix} Cl_2 \\ O \end{smallmatrix} \right\}$. (Malaguti.)

Chlorine and Acetate of Methylene.—By the action of chlorine on acetate of oxide of methyle, there is formed acetate of oxychloride

of formyle, $\text{AcO}_3, \text{C}_2\text{H} \left\{ \begin{smallmatrix} \text{Cl}_2 \\ \text{O} \end{smallmatrix} \right\}$. (Malaguti.) This is a colourless oily liquid, sp. gr. 1.25; boiling at about 298° . Water converts it into acetic and hydrochloric acids. Alkalies produce with it formiate and acetate of the alkali, and chloride of the metal.

By distilling a mixture of hydrochloric acid, peroxide of manganese, and pyroxylic spirit, Aimé obtained a yellow oily liquid, which became colourless by washing with water. Of the nature of this liquid nothing is known.

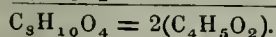
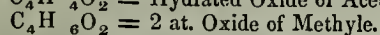
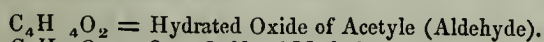
The same chemist has stated that a mixture of pyroxylic spirit, nitric acid, and iodine, left to itself, deposits yellow crystals. If bromine be employed, a heavy oily liquid is formed. Of these compounds nothing further is known.

We are equally destitute of information in regard to the nature of an oily liquid which Aimé has obtained by passing chlorine through a solution of cyanide of mercury in pyroxylic spirit, aiding the reaction by a gentle heat. Without giving the details of his analyses, Aimé has assigned to this substance the formula $2\text{MeO}, \text{CyCl}$; of the accuracy of which there is no evidence.

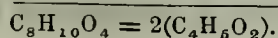
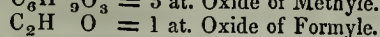
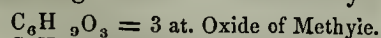
PRODUCTS OF THE DISTILLATION OF WOOD, OF UNCERTAIN CONSTITUTION.

In the examination of a pyroxylic spirit from a manufactory of pyroligneous acid at Wallwyl, Liebig obtained a colourless inflammable liquid, sp. gr. 0.864, having a penetrating ethereal smell and a pungent taste, miscible in all proportions with water. It dissolved chloride of calcium in all proportions, forming a syrupy liquid.

The analyses of this liquid by Liebig and Kane agreed pretty nearly with the formula $\text{C}_4\text{H}_5\text{O}_2$. L. Gmelin obtained results agreeing better with the formula $\text{C}_8\text{A}_9\text{O}_4$; but as there is no proof of the purity or identity of the liquids analyzed, no certain conclusions can be drawn from these experiments. According to the first formula, this substance might be a compound of 1 at. aldehyde and 2 at. oxide of methyle:



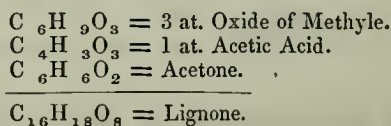
Or it might contain 3 at. oxide of methyle and 1 at. of an oxide of formyle corresponding to the oxide of acetylene:



One circumstance speaks in favour of the first explanation; namely, that the raw pyroxylic spirit contains free aldehyde, which was extracted from it by Scanlan by means of repeated rectifications. The observation of Scanlan has been confirmed by Liebig, Kane, and Gregory, all of whom obtained aldehydammonia in abundance by the addition of ammonia to the liquid prepared by Scanlan. Moreover, this peculiar pyroxylic spirit, when acted on by potash, gave a thick brown mass, very similar to the resin of aldehyde.

Löwig, Weidmann, and Schweitzer, in examining this liquid, found that, when distilled with sulphuric acid and oxalate of potash, it yielded, among other products, oxalate of methyle and acetic acid. Should this observation be confirmed, it will give additional probability to the view according to which it contains aldehyde and oxide of methyle.

Adopting the formula $C_8H_9O_4$ or $C_{16}H_{18}O_8$, this liquid, named *Lignone* by Gmelin, might contain acetone along with a tribasic acetate of methyle analogous to acetal, which may be regarded as a tribasic acetate of ethyle:



At all events, lignone appears to contain some compound of oxide of methyle.

The raw pyroxylic spirit made in Paris contains, according to L. Gmelin, a certain quantity of acetone.

Berzelius considers lignone as a mixture of pyroxylic spirit and acetate of methyle. It is much to be desired that this substance should be thoroughly investigated. Hitherto it has only occurred accidentally in some manufactories, and the circumstances which determine its production are unknown.

CETYLE.

Formula, $C_{32}H_{33}$. Symbol, Ct. The hypothetical radical termed *Cetyle* combines with 1 at. oxygen to form the *oxide of cetyle*. The hydrate of this oxide corresponds to alcohol, and has long been known under the name of *Ethal*. It was discovered by Chevreul, who also detected its analogy to alcohol, and named it from the first syllables of the words ether and alcohol. The researches of Dumas and Peligot have confirmed the opinion of Chevreul. These chemists have produced the chloride of cetyle and the bisulphate of oxide of cetyle, belonging to the same series; and we owe to them also the first rational

formula for spermaceti, the only substance in which the oxide of cetylc has yet been found. They considered it a compound of 2 at. margarate of oxide of cetylc and 1 at. oleate of oxide of cetylc. But L. Smith has recently proved that it contains neither margaric nor oleic acid, and is a pure compound of cetylic acid (ethalic acid) with oxide of cetylc. (See Spermaceti.) It is called *Cetine*.

Hydrate of Oxide of Cetylc. Syn. Ethal.—Formula, $C_{32}H_{33}O + HO = CtO, HO$. (Chevreul, Dumas, and Peligot.) It is best obtained by fusing purified spermaceti (cetine) with half its weight of hydrate of potash at a heat between 212° and 230° . The cetylic acid combines with potash, while ethal is separated. The mass is dissolved in hot water, and hydrochloric acid added in excess; an oily mass rises to the surface, which is a mixture of cetylic acid, ethal, and undecomposed cetine. It is again fused with potash, and the mass, after being dissolved in hot water, is mixed with chloride of calcium, which throws down cetylate of lime, to which the ethal adheres. The precipitate is dried, and treated with hot alcohol, which dissolves the ethal. The cetylate of lime is thrown on a filter, and washed with warm alcohol, and finally with ether, to remove all traces of ethal. The cetylate of lime, decomposed by hydrochloric acid, yields hydrated cetylic acid. The filtered liquids, united and distilled, leave the ethal or hydrated oxide of cetylc, which is purified from a little cetylate of lime by solution in cold ether.

Ethal forms a solid white crystalline mass, fusible below 118° , and solidifying at that temperature. A boiling alcoholic solution deposits crystalline plates. It may be distilled without change. When heated with water, it volatilizes along with the vapour of water. It is neutral, has neither taste nor smell, and burns like wax. It is insoluble in water, soluble in alcohol and ether. Nitric acid decomposes it. Strong sulphuric acid, with the aid of heat, converts it into bisulphate of oxide of cetylc. It does not combine with alkalis.

Chloride of Cetylc.—Formula, $C_{32}H_{33}Cl = CtCl$. (Dumas and Peligot.) Obtained by heating ethal with perchloride of phosphorus. It is an oily liquid, the composition of which agrees with the above formula, but its properties have not been particularly examined.

Bisulphate of Oxide of Cetylc.—This compound has not yet been obtained in a separate form. It is formed when ethal is heated with sulphuric acid, and the mixture yields double salts. Probable formula, $2SO_3, CtO + aq$.

Double Sulphate of Potash and Oxide of Cetylc.—Formula, $2SO_3, CtO, KO$. The mixture of ethal and sulphuric acid is dissolved in alcohol, and neutralized by an alcoholic solution of potash. Sulphate

of potash is precipitated, and the double sulphate remains dissolved. It is purified by repeated crystallization, and forms white pearly scales. (Dumas and Peligot.)

PRODUCTS OF THE DECOMPOSITION OF HYDRATE OF OXIDE OF CETYLE.

Cetene.—Formula, $C_{32}H_{32}$. (Dumas and Peligot.) Obtained by distilling ethal repeatedly with glacial phosphoric acid, which deprives it of 2 at. water, leaving cetene. It is an oily colourless liquid, insoluble in water, soluble in alcohol and ether. It burns with a smoky flame. It boils at 527° . The density of its vapour was found = 8.007, representing 4 volumes. By calculation it is $\frac{31.372}{4} = 7.843$. This compound has the same relation to ethal that olefiant gas, with which it is polymeric, has to alcohol.

AMYLE.

Formula, $C_{10}H_{11}$. Symbol, Ayl. The name of *Amyle* has been given to the hypothetical radical of a series of compounds; one of which, the hydrated oxide of amyle, has been long known as the oil of potato spirit. This compound was first analyzed by Dumas, and since minutely investigated by Cahours.

The following are the compounds established by Cahours:—

- $C_{10}H_{11}$ = Ayl. Amyle, unknown in a separate form.
- $C_{10}H_{11}O$ = AylO. Oxide of Amyle, unknown in a separate form.
- $C_{10}H_{11}O, HO$ = AylO, HO. Hydrated Oxide of Amyle, Oil of Potato Spirit.
- $C_{10}H_{11}Br$ = AylBr. Bromide of Amyle.
- $C_{10}H_{11}I$ = AylI. Iodide of Amyle.
- $C_{10}H_{11}O, 2SO_3, HO$ = AylO, $2SO_3$, HO. Bisulphate of Oxide of Amyle.
- $C_{10}H_{11}O, 2SO_3, BaO$ = AylO, $2SO_3$, BaO. Sulphate of Baryta and Oxide of Amyle.
- $C_{10}H_{11}O, C_4H_3O_3$ = AylO, AcO_3 . Acetate of Oxide of Amyle.

Hydrate of Oxide of Amyle. *Syn.* *Oil of Potato Spirit*; *Amilic Alcohol*; *Bihydrate of Amilene*.—Formula, $C_{10}H_{12}O_2 = C_{10}H_{11}O + HO = AylO + HO$. This compound was first observed by Scheele in the spirit (brandy) obtained from potatoes. It has been examined by Pelletan, Dumas, and Cahours.

When the spirits from potatoes are distilled, there appears, towards the end of the operation, a milky liquid, which, after standing for some time, deposits the oil in question, mixed with water and alcohol. To purify it, it is agitated with water, dried by means of chloride of calcium, and re-distilled. As soon as the boiling point rises to 270° , the hydrated oxide of amyle distils quite pure. (Cahours.)

It is a colourless liquid, very mobile, but yet oily in appearance.

It has a strong smell, which at first is pleasant, but becomes afterwards extremely nauseous. When the vapour is inhaled, it causes asthmatic pains, cough, and even vomiting. Its taste is very acrid. It burns with a bluish-white flame; it boils at 270° ; its sp. gr. is 0.8124 at 60° . The density of its vapour is $= 3.147$, representing 4 volumes. At -4° it solidifies, forming crystalline plates. It produces a stain on paper, which disappears after a short time. It dissolves sparingly in water, to which it communicates its odour; and is miscible in all proportions with alcohol, ether, fixed and volatile oils, and strong acetic acid. It dissolves sulphur, phosphorus, and iodine, without being altered by them. It may also be mixed with a solution of caustic potash, or soda, without change; but, when heated with dry potash, hydrogen is disengaged, and valerate of potash is formed. (Dumas and Stas.) It absorbs a large quantity of hydrochloric acid gas, with evolution of heat. When mixed with oil of vitriol, a violet colour appears, and the bisulphate of oxide of amyle is produced. When distilled with dry phosphoric acid, a carbo-hydrogen is obtained, to which Cahours has given the name of *Amilene*. According to Gerhardt, bichloride of tin combines with the hydrated oxide of amyle, forming a crystalline compound, which is slowly resolved in the air, and more rapidly when in contact with water, into its component parts—bichloride of tin and hydrated oxide of amyle. The chloride of amyle has not yet been formed.

Bromide of Amyle. Syn. Hydrobromate of Amilene.—Formula, $C_{10}H_{11}Br = AylBr$. (Cahours.) Obtained in the same way as the iodide, next to be described. It is an oily volatile liquid, heavier than water, having an acrid taste and a very penetrating alliaceous smell. It may be distilled without change. An alcoholic solution of caustic potash or soda decomposes it with great facility.

Iodide of Amyle. Syn. Hydriodate of Amilene.—Formula, $C_{10}H_{11}I = AylI$. (Cahours.) To prepare this compound, heat is applied to a mixture of 8 parts of iodine, 15 of hydrated oxide of amyle, and 1 of phosphorus. The product is washed with water, dried by means of chloride of calcium, and rectified.

It forms a colourless liquid, heavier than water, having a pungent taste and an alliaceous odour. Light decomposes it, setting free iodine. Alkalies act on it as on the preceding compound. The density of its vapour has been found $= 6.675$. By calculation it is $\frac{27.342}{4} = 6.835$.

Bisulphate of Oxide of Amyle. Syn. Sulphoamylic Acid.—When the double sulphate of baryta and oxide of amyle is dissolved in water, and the baryta separated by sulphuric acid, this compound remains in solution, which may be obtained in the form of a syrupy acid liquid

by evaporation in vacuo, and occasionally deposits fine acicular crystals. It has not been obtained, however, in a state of purity. When mixed with alkalis, double salts are formed. If its solution be boiled, it is resolved into free sulphuric acid, which may now be detected by baryta; and hydrated oxide of amyle, which separates as an oily stratum. Formula, $2\text{SO}_3, \text{AylO}, \text{HO}$.

Sulphate of Potash and Amyle.—Formula, $\text{AylO}, \text{KO}, 2\text{SO}_3$. Obtained by adding carbonate of potash to the double salt of baryta. It forms white needles, or scales, very soluble in water and in alcohol, and very bitter to the taste.

Sulphate of Baryta and Amyle.—Formula of the crystallized salt, $\text{AylO}, \text{BaO}, 2\text{SO}_3, + 3\text{aq.}$: of the salt dried at 212° , $\text{AylO}, \text{BaO}, 2\text{SO}_3 + 2\text{aq.}$ To prepare it, equal parts of oil of vitriol and of hydrated oxide of amyle are mixed. Combination takes place, attended with production of a violet colour. The mixture is neutralized by carbonate of baryta, which causes a precipitate of sulphate of baryta, while the double salt remains in solution. The solution, after being decolorized by animal charcoal, is evaporated till it crystallizes. The salt appears in pearly scales, very soluble in water and alcohol, and bitter to the taste. Its solution is decomposed by boiling, yielding sulphate of baryta, free sulphuric acid, and hydrated oxide of amyle. The dry salt is decomposed by a heat of 392° .

With oxide of lead and with lime, analogous compounds may be formed. The former is represented by the formula $\text{AylO}, \text{PbO}, 2\text{SO}_3 + 2\text{aq.}$; the latter by $\text{AylO}, \text{CaO}, 2\text{SO}_3 + 2\text{aq.}$ The latter appears to be more soluble in cold than in hot water. The solutions of both are decomposed by boiling, exactly like the salt of baryta.

Acetate of Oxide of Amyle. *Syn. Acetate of Amilene.*—Formula, $\text{C}_{10}\text{H}_{11}\text{O}, \text{C}_4\text{H}_3\text{O}_3 = \text{AylO}, \text{AcO}_3$. (Cahours.) It is easily obtained by distilling a mixture of 2 parts of acetate of potash, 1 of hydrated oxide of amyle, and 1 of oil of vitriol. The product, after being dried by means of chloride of calcium, and rectified along with oxide of lead, yields the acetate in a state of purity. It is a colourless liquid, having an ethereal and aromatic odour, insoluble in water, boiling at 248° .

PRODUCT OF THE OXIDATION OF HYDRATED OXIDE OF AMYLE.

Valerianic Acid.—Formula, $\text{C}_{10}\text{H}_9\text{O}_3 + \text{aq.}$ (Ettling, Dumas, and Stas.) When hydrated oxide of amyle is heated along with fused potash, hydrogen is disengaged, and a salt of potash is produced, the acid of which is identical in all respects with that extracted from the root of *Valeriana officinalis* by distilling it with water. To extract the

acid from the product of the distillation of the root with water, it is acted on by caustic potash, which separates a volatile oil. By evaporating the mixture this oil is dissipated; and the dry residue, treated with diluted sulphuric acid, and again distilled, yields an aqueous solution of valerianic acid.

When separated from the water, valerianic acid forms a limpid oil, having a strong and offensive smell of valerian. Its sp. gr. is 0.944; it boils at 270° , is inflammable, and burns with a white smoky flame. It is miscible in all proportions with alcohol, ether, and oil of turpentine. With bases it forms soluble salts, which have a sweet taste. Some of these salts, more particularly the valerianate of zinc, have been introduced into medicine.

The very interesting fact of the formation of this acid by the action of caustic potash on the hydrated oxide of amyle was first observed by Dumas. The reaction is exactly analogous to that by which the hyduret of benzoyle is transformed into benzoic acid; that is, 2 equivalents of hydrogen in the hydrated oxide of amyle are replaced by 2 eq. of oxygen.

PRODUCTS OF THE ACTION OF ANHYDROUS PHOSPHORIC ACID AND OF CHLORINE ON THE HYDRATED OXIDE OF AMYLE.

A. Action of Phosphoric Acid.—When the hydrated oxide of amyle is repeatedly distilled with anhydrous phosphoric acid, a colourless liquid is obtained, containing no oxygen, lighter than water, and possessed of a peculiar aromatic odour. This substance, to which Cahours has given the name of *Amilene*, boils at 320° . The density of its vapour was found equal to 5.061. This corresponds to the calculated density, $\frac{9.8038}{2} = 4.90$, if we consider it to represent two volumes, according to the formula $C_{10}H_{10}$. It has the same composition in 100 parts as hyduret of acetylene (olefiant gas), etherine, and cetene.

B. Action of Chlorine.—When a current of chlorine is passed through the hydrated oxide of amyle, it blackens with disengagement of hydrochloric acid gas. When the action is completed, there is obtained a brown oily liquid, heavier than water. To render it neutral, it is washed with a solution of carbonate of soda, and afterwards with water. It boils at 356° , is insoluble in water and in alkalies, soluble in alcohol and ether. These solutions do not cause a precipitate in nitrate of silver till after some time. The analyses of this compound made by Cahours have led him to adopt the formula $C_{20}H_{17}Cl_3O_4$. He has given to it the name of *Chloramilal*, from a supposed analogy to chloral.

GLYCERYLE.

Formula, $C_6H_7 = Gl$. Chemists have long been acquainted with a substance named Glycerine, which is the hydrate of an organic oxide, and which is met with abundantly in nature; forming, in combination with certain acids, the numerous class of solid and liquid bodies known under the name of fats and fixed oils. Glyceryle is the hypothetical radical of this oxide. The oxide of glyceryle is a compound of this radical with 5 at. oxygen. It is known only in combination with water and acids.

Hydrated Oxide of Glyceryle.—*Syn. Glyceryle; Sweet Principle of Oils.*—Formula, $C_6H_7O_5 + aq.$ (Chevreul; Pelouze.) This substance was discovered by Scheele, who gave it the latter appellation. Chevreul first ascertained its importance, and shewed how extensively it occurs. It is to Chevreul and Pelouze that we owe exact experiments in regard to the constitution of this substance.

The hydrated oxide of glyceryle is contained in the fatty oils and fats, in combination with oleic, stearic, and margaric acids. To separate it, these bodies are boiled with water and powerful bases, which combine with the acids just mentioned, forming soaps. The newly formed salts are next decomposed by tartaric or sulphuric acid, which separate the oily acids; while an aqueous solution is obtained, containing the alkaline salt along with the glycerine. The mixture is evaporated to dryness, and treated with cold alcohol, which dissolves the glycerine, and leaves the alkaline tartrate of sulphate undissolved.

The most convenient and productive method is to saponify linseed oil by means of litharge and a little water. The glycerine is dissolved by the water, and is purified from oxide of lead by a current of sulphuretted hydrogen; while the oxide of lead forms an insoluble soap, or plaster, with the oily acids.

If the solution of glycerine be coloured, it may be decolorized by animal charcoal. It is then evaporated in vacuo over sulphuric acid. When dry, the hydrated oxide of glyceryle forms a syrupy liquid, inodorous, but very sweet to the taste. Its sp. gr. is from 1.252 to 1.27. It is miscible, in all proportions, with water and alcohol; insoluble in ether. It volatilizes to a slight degree with the vapour of boiling water. It cannot be distilled without decomposition. It is inflammable, burning with a luminous flame.

Nitric acid converts it into oxalic acid; peroxide of manganese with sulphuric acid converts it into formic and carbonic acids. When boiled with sulphate of copper, it reduces the copper to the metallic state. Its solution keeps well, and is not fermentescible.

It combines with sulphuric acid, producing bisulphate of oxide of glyceryle. It combines also with potash and baryta; and dissolves, with the aid of heat, the oxide of lead, all deliquescent salts, the sulphates of potash, soda, and copper, and the nitrates of potash and silver.

Chlorine and bromine destroy it; the latter with evolution of heat. When water is added to this mixture, there are obtained an aqueous solution of hydrobromic acid, and a heavy oily liquid, soluble in alcohol and ether, the composition of which is represented by the formula $C_{12}H_{11}O_{10}Br_3$. Gaseous chlorine converts glycerine into a white solid body, $C_{12}H_{11}O_{10}Cl_3$, which has a pleasant ethereal smell, and a taste at once astringent, acid, and bitter.

It has been observed that the glycerine of different fats does not exhibit the same composition. According to Stenhouse the glycerine of palmitine is $C_6H_4O_2$; and Playfair obtained a similar formula, or the half of it, for the glycerine of myristine. In these cases, however, the sweet principle, when separated from the oily acid, always appears as ordinary glycerine. It is only as existing in the fats that they exhibit a different composition. It will be seen that these differ from the formula above given in the proportion of water, for $C_6H_4O_2 + 4HO = C_6H_7O_5.HO$. Berzelius has proposed to admit, as the radical of these compounds, the combination C_3H_2 , which he calls lipyle. The glycerine of myristine will then be oxide of lipyle, C_3H_2O ; that of palmitine will be polymeric with it, or $2(C_3H_2O) = C_6H_4O_2$, while the glycerine of common fats will be $2(C_3H_2O) + 3HO = C_6H_7O_5$, which, when separated, takes up 1 eq. of water, to form the hydrated oxide of glyceryle, or glycerine. We shall see that Redtenbacher has obtained from glycerine a compound $C_6H_4O_2$, which, however, does not appear to be the body existing in palmitine or myristine.

Acroleine.—When fats are distilled, there is formed a volatile product of the most remarkable pungency, the nature of which has been recently ascertained by Redtenbacher. He found that it is derived from glycerine alone; and, after overcoming almost insuperable obstacles, arising from the frightful effects of the vapour on the eyes, as well as from its extreme proneness to change, he succeeded in isolating the pungent principle, which had been named acroleine, but to which he gave the name of hydrated oxyde of acryle.

Acryle.—This name is given to the hypothetical radical of acroleine, not yet isolated. Its formula is C_6H_3 .

Hydrated Oxide of Acryle. *Syn. Acroleine*.—Best obtained by distilling glycerine with anhydrous phosphoric acid, in an atmosphere of carbonic acid, to prevent oxidation. When rectified it is a very

fluid, transparent oil, of the most astonishing pungency, so that a few drops, allowed to evaporate in a large room, will cause in the eyes of all present a flow of tears, with severe pain. It attracts oxygen much more rapidly even than aldehyde; and, like that body, passes into an acid, very analogous to acetic acid, the acrylic acid. Acroleine boils at 125° , and is very soluble in ether, sparingly so in water. Its formula is C_6H_3O,HO . It is very apt, like aldehyde, to change spontaneously into a white solid, which Redtenbacher calls Disacryle, and considers to be $C_{10}H_7O_4$. But as this change goes on in closed tubes, it is probably an isomeric modification, like that of aldehyde. It is remarkable that acroleine, derived from glycerine, has the composition of the glycerine in palm oil.

Acrylic Acid.—Acroleine when oxidized is converted into this acid, very analogous to acetic acid. Its formula is $C_6H_3O_3,HO$. When glycerine is heated with potash, acrylic acid appears to be formed, but is soon destroyed, and in its place are found acetic and formic acids. This is easily explained; for 1 eq. of anhydrous acrylic acid, with 6 eq. of water, contain the elements of 3 eq. formic acid; 2 eq. of acrylic acid, with 3 eq. of water, contain those of 2 eq. of acetic acid; or, lastly, 1 eq. of acrylic acid, with 1 of water and 2 of oxygen, may yield 1 of acetic acid, and 1 of formic acid. The following table will show the analogy between acryle and acetyle:—

Acryle	C_6H_3	= Acr, unknown.
Hydrated Oxide of Acryle	C_6H_3O, HO	= $AcrO,HO$, Acroleine.
Acrylous Acid . .	$C_6H_3O_2,HO$	= $AcrO_2,HO$, uncertain.
Acrylic Acid . . .	$C_6H_3O_3,HO$	= $AcrO_3,HO$.

It is worthy of notice, that, when a solution of glycerine, $C_6H_7O_5,HO$, is made to ferment with yeast, it yields metacetic acid, $C_6H_5O_3,HO$, evidently by losing 2 eq. of water. This last acid differs from acrylic acid by containing 2 eq. of hydrogen more, while acetic acid differs from acrylic acid by containing 2 eq. of carbon less.

Bisulphate of Oxide of Glyceryle. Syn. Sulphoglyceric Acid.—Formula, $2SO_3, C_6H_7O_5 + aq$. When 1 part of oil of vitriol is mixed with $\frac{1}{2}$ of glycerine, combination takes place with much evolution of heat, but without blackening. According to Pelouze and Frémy, the same compound is obtained when oils and fats are acted on by oil of vitriol. To obtain it in a state of purity, a solution of the double sulphate of lime and glyceryle is carefully precipitated by oxalic acid. It is a very sour liquid, which undergoes spontaneous decomposition, and therefore precipitates the salts of baryta. It is decomposed very rapidly by a gentle heat.

The double salts of glyceryle are obtained by adding the bases to

the mixture of sulphuric acid and glycerine. These double sulphates are sometimes called sulphoglycerates. Those of lime and baryta are very soluble and crystallizable. When their solutions are boiled, they are resolved into sulphates of the metallic oxides, and hydrated oxide of glycyle.

Sulphate of Lime and Glycyle.—Formula, $\text{CaO}, \text{C}_6\text{H}_7\text{O}_5, 2\text{SO}_3$. (Pelouze.) Obtained as above described. It forms white needles and scales, soluble in half their weight of water, insoluble in alcohol and ether. At a heat of about 800° it is decomposed, yielding vapours of a very disagreeable smell, which irritate the eyes powerfully. The residue contains carbon and sulphate of lime.

Sulphate of Lead and Glycyle, according to Pelouze, has a composition analogous to that of the preceding salt.

It is probable that the oxide of glycyle exists in nature, combined with other acids besides the fatty acids. Such compounds are well worthy of examination. Thus, for example, the benzoate of oxide of glycyle would have the composition of *picROTOXINE*; in like manner, mannite may be another oxide of glycyle $= \text{C}_6\text{H}_7\text{O}_6 = \text{GlO}_6$.

ALLYLE.

This name is given to the supposed radical of certain volatile oils, as those of garlic (*Allium sativum*), of *Cochlearia armoracea*, *Alliaria officinalis*, *Ferula assafoetida*, and mustard (*Sinapis nigra*). This radical is not yet known in a separate state. Its oxide has been shewn by Wertheim to exist. The formula of the radical is C_6H_5 ; and the following table contains the names and formulæ of the compounds hitherto described:—

Allyle	C_6H_5	= All.
Oxide of Allyle .	$\text{C}_6\text{H}_5\text{O}$	= AllO.
Sulphuret of Allyle	$\text{C}_6\text{H}_5\text{S}$	= AllS.
Sulphocyanide of Allyle	$\text{C}_6\text{H}_5 + \text{C}_2\text{NS}_2$	= AllCyS ₂ .

The sulphuret constitutes the oils of garlic and assafoetida; and the sulphocyanide those of mustard, of *Alliaria officinalis*, and of *Cochlearia armoracea* and *officinalis*.

These oils will be hereafter described: they are here mentioned in connexion with the radical allyle, the existence of which is highly probable, although it has not yet been isolated, because the sulphuret and sulphocyanide, as well as the oxide, are mutually convertible, proving the permanency of the group C_6H_5 .

It may here be mentioned, that the radical allyle only differs from metacetic acid, $\text{C}_6\text{H}_5\text{O}_3$, by 3 eq. of oxygen. Hydrated oxide of

allyle may therefore prove to be the aldehyde of this series, as aldehyde itself is of the series of acetyl^e, and acroleine of that of acryle. Although the existence of oxide of allyle has been proved, its properties are not yet ascertained.

In the preceding pages of the Organic Chemistry, those substances have been grouped together which stand to each other in a fixed and known relation, either with regard to their formation or their composition.

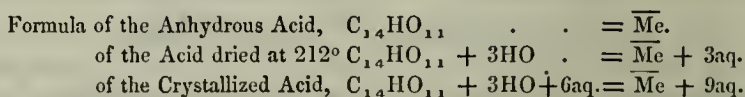
In the remaining part of this work we shall describe those organic compounds concerning the radicals of which nothing certain is yet known.

These compounds will be described in the order of their composition. The tribasic acids, or those which in one atom contain the equivalent of three atoms of base, will be first considered. After these will follow the bibasic; and, lastly, the monobasic acids. The tribasic and bibasic acids frequently yield pyrogenous acids, or pyroacids, when decomposed by heat. These will be treated of as products of the decomposition of the acids which yield them.

Many of the compounds now to be described are products of the oxidation of other substances, not acid; these will be noticed in connexion with the acids they produce, so that the substances which have a natural connexion will be grouped together, as in the case of the substances already described.

MECONIC ACID.

A tribasic acid. Symbol, $\overline{\text{Me}}$.



Seguin first observed that infusions of opium strike a blood-red colour with persalts of iron. Sertuerner first obtained a meconic acid (pyromeconic acid) by decomposing meconate of baryta with sulphuric acid, and subliming the acid obtained. Robiquet, in 1832, shewed that the acid existing in opium differed from the sublimed acid, obtained it in a state of purity, and discovered the komeenic acid.

To prepare meconic acid, pure bibasic meconate of potash is dissolved in 16 to 20 parts of hot water, and 2 to 3 parts of strong hydrochloric acid are added. On cooling, a quantity of crystals is deposited,

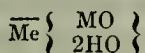
chiefly acid meconate of potash; these are treated a second time with water and hydrochloric acid, by which the potash is entirely removed. The crystals should leave no residue when heated on platinum foil. Boiling with hydrochloric or other acids must be avoided, as the acid is thus changed into komeinic acid.

Meconic acid forms beautiful pearly scales, of a sour and astringent taste. They lose, when heated, 21 p. c. of water = 6 aq., and become opaque. The crystals are sparingly soluble in cold water, much more so in hot water. When the solution is boiled for a long time, the acid is destroyed; and komeinic acid, oxalic acid, carbonic acid, and a deep brownish-yellow colouring matter, are formed. When boiled with strong hydrochloric acid, komeinic and carbonic acids alone are formed. Animal charcoal absorbs meconic acid, and cannot be used to decolorize it. When the acid is exposed to heat, at 248° it is decomposed, yielding water and carbonic acid, while komeinic acid is left. If the heat be increased, the komeinic acid is resolved into pyromeconic and carbonic acids. Sulphuric acid acts on meconic acid in the same way as hydrochloric acid, but more slowly. Nitric acid decomposes it very rapidly. When boiled with an excess of caustic potash, meconic acid is entirely resolved into oxalic acid, carbonic acid, and a brown matter. (Liebig.) The persalts of iron are coloured of a deep blood-red by meconic acid or its salts. The acid is soluble in alcohol.

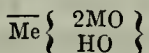
MECONATES.

Meconic acid forms with bases three kinds of salts, according as 1, 2, or 3 eq. of the hydratic water are replaced by metallic oxides. The general formulæ for these salts are as follows:—

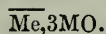
Monobasic Salts.



Bibasic Salts.



Tribasic Salts.



The only tribasic salt yet analyzed is one formed with oxide of silver. All the soluble monobasic and bibasic meconates have an acid reaction: the soluble tribasic salts have an alkaline reaction. The monobasic and bibasic salts of the alkalies and alkaline earths are sparingly soluble or insoluble; the tribasic are very soluble.

Meconate of Ammonia.—The monobasic and bibasic meconates of ammonia are crystallizable and have an acid reaction. An excess of ammonia produces tribasic meconate, which gives to the liquid a yellow colour.

Meconates of Potash.— $\overline{\text{Me}}, 2\text{KO}, \text{HO}$. The bibasic salt is obtained

by adding caustic potash to a mixture of water with the impure meconic acid obtained from the meconate of lime, (see below,) till a greenish colour begins to appear. Heat is applied till the whole is dissolved; and, on cooling, the salt crystallizes in large quantity. It is purified by pressure and repeated crystallization. It is sparingly soluble in cold water. Caustic potash, added to its solution, produces a soluble tribasic salt, which is yellow. If boiled with excess of potash, it is converted into oxalate and carbonate, while an intense colouring matter is formed. If treated with hydrochloric acid, it yields monobasic meconate in shining needles, $= \overline{\text{Me}}, \text{KO}, 2\text{HO}$.

Meconates of Soda.—In all respects analogous to the meconates of potash.

Meconates of Lime.—The insoluble bibasic meconate of lime is easily obtained from opium by adding chloride of calcium to the infusion of that drug, as in the process of Gregory and Robertson for preparing muriate of morphia. Its formula is $\overline{\text{Me}}, 2\text{CaO}, \text{HO} + 2\text{aq}$. It is used for preparing meconic acid by the following process, which is a modification of Robiquet's, proposed by Gregory. (Ann. der Pharm. xxiv. 43.) One part of the salt is mixed with 20 of water at 212° , and 3 parts of strong hydrochloric acid are added; the whole dissolves, and on cooling deposits monobasic meconate of lime, $\overline{\text{Me}}, \text{CaO}, 2\text{HO} + \text{aq}$., in silvery crystals. The sulphate of lime, which is always contained in the meconate of commerce in large quantity, is entirely retained in solution by the large excess of hydrochloric acid prescribed, which has also this advantage, that it causes the acid meconate of lime and the meconic acid to crystallize out almost entirely, hardly any being retained in solution. The crystals obtained in the first operation are again treated exactly in the same way, boiling being avoided; and the operation is repeated, if necessary, till the crystals, heated on platinum foil, leave no residue of lime. They are then coloured meconic acid, which is purified by being converted into meconate of potash, as above described; and from the pure meconate of potash the acid is extracted by a similar process, as already mentioned.

The *Meconates of Baryta, Magnesia, and Protoxide of Iron* have been described, but have little interest.

Meconate of Peroxide of Iron.— $\overline{\text{Me}}, \text{Fe}_2\text{O}_3$? This is a very soluble salt, of a deep red colour. Sulphurous acid and protochloride of tin decolorize it, especially with the aid of light. Owing to the intensity of its colour, the persalts of iron may be employed as tests for meconic acid, and hence of opium, the only substance in which meconic acid occurs.

Meconate of Lead.— $\overline{\text{Me}}, 2\text{PbO}, \text{HO}$. A white insoluble powder, sometimes used in preparing meconic acid.

Meconates of Silver. Bibasic.— $\overline{\text{Me}}, 2\text{AgO}, \text{HO}$. This salt is obtained by adding nitrate of silver to a solution of meconic acid. It is a heavy, white, insoluble powder. When boiled with water, it forms a yellow tribasic salt, while the water dissolves meconic acid. If heated, it leaves brilliant metallic silver. When boiled with diluted nitric acid, it yields cyanide of silver. (Liebig.)

Tribasic.— $\overline{\text{Me}}, 3\text{AgO}$. Meconic acid, slightly supersaturated with ammonia, gives with nitrate of silver a yellow precipitate of tribasic meconate of silver. (Liebig.)

KOMENIC ACID.

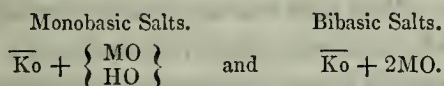
A product of the decomposition of meconic acid. A bibasic acid. Discovered by Robiquet. Formula of the crystallized acid, $\text{C}_{12}\text{H}_2\text{O}_8 + 2\text{HO}$. (Liebig.)

Komenic acid is formed from meconic acid, by the influence of heat, or the reaction of a powerful acid. It is also formed by simply boiling meconic acid with water; but in this way it is accompanied by an intense brown colouring matter, formed along with it. When meconic acid is boiled with strong hydrochloric acid, komenic acid is obtained almost colourless. The two acids have a close relation to each other. Meconic acid, containing its basic water, $\text{C}_{14}\text{H}_4\text{O}_{14}$, by losing 2 at. water, 2HO , and 2 at. carbonic acid, 2CO_2 , is converted into komenic acid, $\text{C}_{12}\text{H}_2\text{O}_8$, which takes up 2 at. of basic water.

Komenic acid forms hard crystalline grains, or crusts; its solution decomposes the carbonates, and produces a blood-red colour with the persalts of iron. When heated to 570° , it is resolved into pyromecconic acid, carbonic acid, and water.

KOMENATES.

Komenic acid forms two sets of salts with bases, the general formulæ of which are,



Of these salts little is known; the monobasic alkaline komenates are less soluble than the bibasic salts of the same bases. The monobasic komenate of silver is white, the bibasic yellow. Both have been analyzed by Liebig. (Ann. der Pharm. xxvi.) Komenate of peroxide of iron forms black crystals, sparingly soluble, the formula of which

is such that they contain 2 eq. of komenic acid, 1 of peroxide of iron, and 7 of water. (Stenhouse.)

PRYOMECONIC ACID.

Formula of the crystallized acid, $C_{10}H_3O_5 + aq.$ (Robiquet.) It was discovered by Sertuerner, and long viewed as sublimed meconic acid, till Robiquet discovered the meconic acid, from which it is produced.

It is best obtained by distilling komenic acid at 570° . The latter, by losing 1 at. water and 2 at. carbonic acid, yields pyromeconic acid; $C_{12}H_4O_{10} = C_{10}H_3O_5 + HO + 2CO_2$. Towards the end of the distillation, feathery crystals of another acid condense in the neck of the retort, which Gregory considers to be komenic acid, perhaps regenerated. At all events, he found its properties very similar to those of komenic acid. Stenhouse considers it to be a distinct acid, isomeric or polymeric with komenic acid, and has named it parakomenic acid. It differs from komenic acid only in its relation to the acetates of lead and of copper, neither of which are precipitated by it, while both are precipitated by komenic acid.

Pyromeconic acid crystallizes easily, either by sublimation or from its solution in alcohol. It is very soluble, and strikes a red colour with the persalts of iron. According to Robiquet, it is so feeble an acid that it crystallizes unchanged out of a solution of potash. Its compound with oxide of lead is $C_{10}H_3O_5, PbO$; so that it seems to be a monobasic acid. Liebig has pointed out that its composition is the same as that of pyromucic acid; but Stenhouse has shewn that their properties are different. He also obtained the pyromeconate of peroxide of iron in small cinnabar-red crystals, containing 1 eq. of the peroxide and 3 of the acid. The pyromeconate of copper forms fine green prisms.

CHELIDONIC ACID.

This acid is found in the juice of *Chelidonium majus*, a plant of the family of the *Papaveraceæ*, which also, like the poppy, contains certain vegetable bases. The acid has lately been investigated by Lerch, who has found it to be a tribasic acid, very analogous to meconic acid.

The expressed juice is heated to coagulate albuminous matter, and precipitated by nitrate of lead, some nitric acid being added to retain in solution malate of lead. The precipitate contains chelidonic acid, combined with oxide of lead and with lime from the juice, and also a little malate of lead. It is decomposed by sulphuretted hydrogen, which gives an acid liquid, free from lead, but still containing lime.

This is neutralized by chalk, and evaporated to a small bulk. It is then filtered hot, when the malate of lime, if any be present, is left on the filter, and the filtered liquid on cooling deposits colourless crystals of chelidonate of lime. This salt is next decomposed by carbonate of ammonia, and the chelidonate of ammonia mixed with an excess of hydrochloric acid, when the chelidonic acid is separated, and forms white needles of a silky lustre.

The formula of the anhydrous acid is $C_{14}H_2O_{10} = \overline{\text{Che}}$. It forms two hydrates: that which crystallizes from a hot solution is $\overline{\text{Che}}, 3\text{HO} + \text{aq.}$; that which forms by slow evaporation is $\overline{\text{Che}}, 3\text{HO} + 2 \text{ aq.}$ When heated to 212° , it loses the water of crystallization, and, besides this, one of the 3 eq. of basic water, this third equivalent being retained by a very feeble affinity.

The salts of this acid are analogous to those of ineconic acid, and assume, like them, three forms, according to the amount of water replaced by the base. In the neutral or tribasic salts, all the basic water is replaced, as in the neutral salt of silver, $\overline{\text{Che}}, 3\text{AgO}$, of baryta, $\overline{\text{Che}}, 3\text{BaO} + 5 \text{ aq., \&c.}$ In the bibasic salts, 2 eq. of basic water are replaced, as in that of lime, $\overline{\text{Che}}, 2\text{CaO}, \text{HO} + 5 \text{ aq.}$; of soda, $\overline{\text{Che}}, 2\text{NaO}, \text{HO} + 7 \text{ aq., \&c.}$; and in the monobasic salts, 1 eq. of basic water only is replaced, as in that of soda, $\overline{\text{Che}}, \text{NaO}, 2\text{HO} + 3 \text{ aq.}$ There are also still more acid salts, as of baryta and soda, which have the formula $\overline{\text{Che}}, \text{BaO}, 2\text{HO} + \overline{\text{Che}}, 3\text{HO} + 2 \text{ aq.,}$ and $\overline{\text{Che}}, \text{NaO}, 2\text{HO} + \overline{\text{Che}}, 3\text{HO} + 3 \text{ aq.}$; and basic salts, as that of lead, $\overline{\text{Che}}, 3\text{PbO} + 3\text{PbO}$. In many of these salts, especially the bibasic, the third basic eq. (of water) is easily expelled by heat, as in the acid itself, leaving a bibasic salt, although the acid is tribasic. Thus, the bibasic salts of lime, oxide of lead, and ammonia, all lose when heated, the two former to 392° , the latter to 212° , the eq. of basic water they contain, leaving the salts $\overline{\text{Che}}, 2\text{CaO}$, $\overline{\text{Che}}, 2\text{PbO}$, and $\overline{\text{Che}}, 2\text{NH}_4\text{O}$.

It is evident, on comparing the formulæ of meconic and chelidonic acids, $C_{14}H_{11}O_{11}, 3\text{HO}$ and $C_{14}H_2O_{10}, 3\text{HO}$, that they are nearly allied; and this also appears from their occurring in the same natural family of plants. It is also not improbable that the kinic and gallic acids, between which a similar relation exists, and which are commonly supposed to contain 7 eq. of carbon, (gallic acid is $C_7H_3O_5$, kinic acid $C_7H_4O_4$.) may really contain 14 eq. of carbon, and thus belong to the same series as meconic and chelidonic acids, with which they seem to be in some way related. (Lerch.)

When chelidonic acid is decomposed by heat, it yields a sparingly

soluble acid, not yet examined, which is probably analogous to komeinic acid, possibly identical with it.

TANNIC ACID.

Syn. Tannin; Acidum Quercitanicum.—Formula, $C_{18}H_6O_9 + 3$ Ho. Symb. $\overline{Qt} + 3aq$. It is found in every part, but especially in the bark, of all species of quercus, but in the greatest quantity in gall-nuts. To obtain it, coarsely powdered gall-nuts are acted on by ether, which has previously been shaken with water, in a percolator. In the bottle placed below are found two strata of liquid. The heavier is a saturated solution of nearly pure tannic acid in water; the lighter is a solution of gallic acid and of colouring matter in ether. The heavier liquid is gently evaporated to dryness, and leaves a shining porous mass of pure tannic acid. (Pelouze.)

It has usually a pale yellow colour, is very soluble in water, and has a purely astringent taste of singular intensity. It reddens vegetable blues. The solution, when heated in contact with air, absorbs oxygen, giving off an equal volume of carbonic acid, and is converted into gallic and ellagic acids. A moderately strong solution, when mixed with sulphuric, hydrochloric, phosphoric, arsenic, and boracic acids, yields precipitates, soluble in pure water and in alcohol, which are compounds of tannic acid with the other acids. (Berzelius.)

If the compound with sulphuric acid be dissolved with the aid of heat in diluted sulphuric acid, and boiled for a few minutes, the tannic acid disappears, and on cooling a large quantity of coloured crystals of gallic acid is obtained. An analogous change occurs when it is boiled with an excess of caustic alkali. (Liebig.)

Tannic acid combines with the skin of animals, forming an insoluble compound which does not putrefy. This is *leather*. By means of a bit of prepared skin, tannic acid may be entirely withdrawn from its solution in water. A solution of gelatine is precipitated by tannic acid in thick flocks, which dissolve when heated with the supernatant fluid. By the action of heat, tannic acid is converted into metagallic and pyrogallic acids.

TANNATES.

These salts are characterized by striking a deep bluish-black colour with the persalts of iron (*ink*). They do not precipitate gelatine till an acid be added. Tannic acid and the soluble tannates precipitate most of the organic alkalies in the form of white pulverulent compounds, insoluble in water, soluble in acetic acid. A solution of tannic acid, neutralized with potash, yields a thick precipitate, easily soluble in ex-

cess of potash; when this alkaline solution is boiled, it produces gallic acid and a brown colouring matter. The cold solution of tannate of potash rapidly absorbs oxygen from the air, and becomes brown.

Ammonia and soda act like potash. The tannates of baryta, strontia, lime, and magnesia are very sparingly soluble. Tannate of alumina is quite insoluble. The salts of protoxide of iron are not altered by tannic acid; but the mixture, when exposed to the air, absorbs oxygen, and becomes black.

The tannates have lately been studied by Büchner, jun., who has shewn that the formulæ of several of them are unusual. *Tannate of potash* forms a crystalline powder, composed of $C_{54}H_{22}O_{34} + 2KO$, which may be considered as an acid tannate, $\overline{Qt}\left\{\begin{smallmatrix} 2KO \\ HO \end{smallmatrix}\right\} + 2(\overline{Qt}, 3HO)$.

Tannate of soda is $4\overline{Qt}\left\{\begin{smallmatrix} NaO \\ 2HO \end{smallmatrix}\right\} + \overline{Qt}, 3HO$. *Tannate of ammonia* is $\overline{Qt}, NH_4O + \overline{Qt}, 3HO$. There are two *tannates of baryta*, in both of which the basic water is retained along with the baryta; they are $4(\overline{Qt}, 3HO) + 3BaO$ and $3(\overline{Qt}, 3HO) + 4BaO$. There are also two *tannates of lead*, $\overline{Qt}, 3PbO$ (Liebig) and $\overline{Qt}\left\{\begin{smallmatrix} HO \\ 2PbO \end{smallmatrix}\right\} + \overline{Qt}, 3HO$.

(Berzelius.) *Tannate of peroxide of iron* is $3(\overline{Qt}, 3HO) + Fe_2O_3$; and *tannate of oxide of antimony* is $3(\overline{Qt}, 3HO) + Sb_2O_3$. (Pelouze.) These facts are sufficient to shew, that, although tannic acid exhibits in a considerable degree the characters of a tribasic acid, yet we cannot consider its relation to bases as fully understood.

The salts of tannic acid require a thorough investigation.

PRODUCTS OF THE DECOMPOSITION OF TANNIC ACID.

It has already been mentioned that tannic acid is readily converted into gallic acid and a brown matter, when boiled with acids or alkalis. The products of the distillation of tannic acid are the same as those of gallic acid; and this circumstance, with some observations of Robiquet, led to the idea that tannic acid contains gallic acid ready formed. An aqueous infusion of nut-galls gradually passes into gallic acid. Hitherto it is impossible to say what is the body which, united with gallic acid, forms tannic acid. According to Braconnot, nut-galls, powdered and moistened, undergo fermentation, yielding alcohol and carbonic acid, which would indicate the presence of sugar, a substance not yet observed in a free state in nut-galls: 3 at. of tannic acid contain the elements of 6 at. of gallic acid and 1 at. of grape sugar.

It is also remarkable, that, according to Pelletier, a mixture of

gallic acid and gum precipitates gelatine, which neither body separately does.

According to Pelouze, when a solution of tannic acid, by absorbing oxygen, is converted into gallic acid, an equal volume of carbonic acid is given off. If 8 at. oxygen be added to 1 at. tannic acid, we have the elements of 4 at. carbonic acid, 2 at. water, and 2 at. gallic acid, $C_{18}H_8O_{12} + O_8 = 4CO_2 + 2HO + 2(C_7H_3O_5)$. According to Erdmann, much ellagic acid is formed in this process. Tannic acid, treated with peroxide of manganese or of lead, is oxidized without the production of gallic acid.

There is reason to think that the brown matter produced when tannic acid is converted into gallic acid by the action of sulphuric acid is a secondary product of the decomposition of a colourless compound produced at first with the gallic acid. If from 1 at. of tannic acid we subtract 2 at. of anhydrous gallic acid, the remainder has the composition of hydrated acetic acid, or of sugar of starch. But acetic acid has been in vain sought for among the products of this reaction; and sugar of starch may be heated with sulphuric acid of the same strength without being decomposed or rendered brown.

The question of the pre-existence of gallic acid in tannic acid is interesting; but it must for the present remain undecided.

Tannoxylic Acid.—When a solution of tannic acid is exposed to the air after being mixed with an excess of potash, it absorbs oxygen from the air, and becomes at last nearly black. If acetate of lead be now added, there is formed a carmine-red precipitate, which contains a new acid, *tannoxylic acid*, which, according to Büchner, jun., has, in the anhydrous state, the formula $C_{15}H_5O_{11}$, and is tribasic, the salt of lead being $C_{15}H_5O_{11}, 3PbO$. In its formation, 1 eq. of tannic acid has absorbed 8 of oxygen, and has yielded 3 eq. of carbonic acid, and 1 eq. of tannoxylic acid. The acid has not been isolated.

Tannomelanic Acid.—When tannic acid is boiled with potash, it absorbs, in the first instance, 8 eq. of oxygen, yielding carbonic acid, water, and gallic acid, as above explained. But if the boiling be long continued, the gallic acid disappears, and there is formed a new acid, tannomelanic acid, which, on the addition of hydrochloric acid, falls as a dark brown, humus-like powder. (Büchner, jun.) Its formula is $C_{14}H_6O_9 = C_{14}H_4O_7, 2HO$, and it is bibasic. This acid may be derived from tannoxylic acid by the absorption of oxygen, and the separation of water and carbonic acid. It may also be derived, in like manner, from gallic acid. In fact, it would appear, from the observations of Büchner, that tannic acid may yield these three acids consecutively, as in the following scheme:—

3 eq. of Anhydrous Tannic Acid	$C_{56}H_{15}O_{27}$
absorb from the air, by exposure along with Potash, 24 eq. of Oxygen	O_{24}
and produce 9 eq. of Carbonic Acid	$C_{56}H_{15}O_{51}$ $C_9 O_{18}$
and 3 eq. Anhydrous Tannoxylic Acid	$C_{42}H_{15}O_{33}$
When boiled with Potash to a certain point, there are given off 3 eq. of Carbonic Acid and 9 of Water	$C_3H_9O_{15}$
and there are formed 6 eq. of Anhydrous Gallic Acid	$C_{42}H_{6}O_{18}$
By continued boiling there are taken up 2 eq. of Water and 22 of Oxygen	$H_{2}O_{24}$
and there are formed 14 eq. of Carbonic Acid	$C_{42}H_8 O_{42}$ $C_{14} O_{28}$
and 2 eq. of Anhydrous Tannomelanic Acid	$C_{28}H_4 O_{14}$

GALLIC ACID.

Formula of the Crystals	$C_7HO_3 + 3HO = \overline{G} + 3aq.$
of the Acid dried at 212°	$C_7HO_3 + 2HO = \overline{G} + 2aq.$
of the Acid in the Salt of Lead, A, $C_7HO_3 + HO = \overline{G} + aq.$	
in the Salt of Lead, B, $C_7HO_3 = \overline{G}.$	

Discovered by Scheele. It exists ready formed in the seeds of the mango, and is a product of the decomposition of tannic acid. Its preparation has been described under Tannic Acid. The coloured crystals are purified by being combined with oxide of lead, and the compound decomposed by sulphuretted hydrogen. Here the sulphuret of lead acts like animal charcoal in removing the colouring matter.

It crystallizes in brilliant prisms, which are white when pure, but are generally of a pale yellow colour. It is soluble both in water and alcohol, and does not precipitate gelatine. Its solution, exposed to the air, absorbs oxygen, gives off carbonic acid, and becomes brown and mouldy. The presence of alkalis hastens this change. Gallic acid colours the persalts of iron of a deep bluish-black, and forms with solutions of black oxide of iron a permanent black precipitate.

When gallic acid is dissolved in oil of vitriol with the aid of heat, it forms a carmine-red solution, which, when thrown into water, deposits a reddish-brown precipitate, which contains no sulphuric acid, and at 212° loses 10 p. c. water. When thus dried, it is gallic acid minus 1 at. basic water and 1 at. water of crystallization. Its formula is $C_7H_2O_4$. (Robiquet.) This substance is insoluble in water, soluble in alkalis. It may be made to yield the same tints to cloth as madder, with the same mordants. When heated, it yields vermilion-coloured crystals. When gallic acid is heated with a solution of

chloride of calcium, carbonic acid is disengaged, and a crystalline powder is deposited, the composition of which is unknown. (Robiquet.)

Heat converts gallic acid into carbonic, pyrogallic, and metagallic acids; and when boiled with potash, it is converted into tannomelanic acid.

GALLATES.

These salts are distinguished by the rapidity with which they are decomposed when exposed to the air in contact with free alkali. When a little gallic acid is added to an alkaline solution, it passes through yellow, green, red, and brown to black. This colour has sometimes erroneously been attributed to the presence of oxide of iron in mineral waters tested by gallic acid.

The gallates have lately been minutely studied by Büchner, jun., who has shewn that the formulæ of these salts are still more anomalous than those of the tannates. The gallates of lead and zinc are bibasic, while the composition of most of the other gallates is strangely varied. For the details of these elaborate researches, the reader is referred to the memoir of Büchner, *Annalen der Chemie und Pharmacie*, liii. 175. The gallates of potash, soda, and ammonia are crystalline and soluble; most of the others are sparingly soluble or insoluble. Gallic acid has a great tendency to form basic compounds, especially with the magnesian class of oxides. On the whole it must be concluded, that, in the present state of our knowledge, these salts cannot be easily reduced to any theory.

ACTION OF HEAT ON GALLIC AND TANNIC ACIDS.

When tannic acid is distilled by a quick fire, it froths and melts into a black viscid liquid, which, after the heat has been continued for some time, becomes solid. The volatile products are carbonic acid, water, and crystals of pyrogallic acid. The solid residue dissolves in alkalis, and is precipitated by acids as a black powder, which Pelouze calls *Metagallic Acid*, but for which Berzelius proposes the name of *Melangellic Acid*.

When gallic acid is kept for a long time at a heat of 410° , it is changed into a grey powder, which dissolves in hot water, and on cooling yields reddish-coloured crystals of an astringent taste. If gallic acid be heated to 440° , it melts, and leaves a shining black mass, which is soluble in water, and tastes like catechu. It precipitates gelatine; but does not, like tannic acid, precipitate the or-

ganic alkalies. At a still higher temperature metagallic acid is formed. The volatile products are the same as those of tannic acid.

PYROGALLIC ACID.

Formula, C_2HO , when reduced to the simplest form. It is uncertain whether its equivalent be $C_6H_3O_3$, or $C_8H_4O_4$. Its preparation by heating tannic or gallic acids has been described.

It forms shining scales or needles, of a bitter and astringent taste; is neutral to test paper, and melts at 240° , boils at 410° , and sublimes unchanged. If suddenly heated to 480° , it is converted into water and metagallic acid; a higher temperature produces carbon and empyreumatic products. It is soluble in water; and reduces gold, silver, and mercury from their solutions. It strikes a bluish-black colour with salts of protoxide of iron, and also with the persalts of iron, which are reduced thereby to protosalts.

Of pyrogallic acid so little is known, that it is even doubtful if it possess acid properties. It stands to gallic acid in the same relation as acetone to acetic acid.

PYROGALLATES.

Of these salts, only the pyrogallate of lead has been examined by Berzelius, Pelouze, and the late R. C. Campbell of Glasgow. According to the two former, the precipitate formed by adding pyrogallic acid to acetate of lead is $C_6H_3O_3 + PbO$. According to Campbell, it is $C_8H_4O_4 + PbO$.

All the salts of pyrogallic acid, in contact with an excess of alkali, undergo a change similar to that of the salts of gallic acid. Pyrogallic acid, neutralized with potash, strikes a deep blue with the persalts, and a bluish-black with the protosalts of iron.

METAGALLIC ACID.

Formula of the anhydrous acid, $C_6H_2O_2$. (Pelouze.) Probable atomic weight, $C_{12}H_3O_3 + HO$.

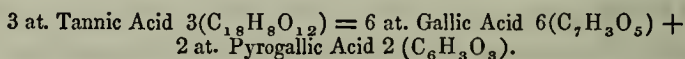
It is a product of the decomposition of tannic, gallic, and pyrogallic acids, and its preparation has been already described.

It forms a black powder, soluble in alkalies. These solutions have a black colour, and cause black precipitates in solutions of lead and silver. The salt of silver is $C_{12}H_3O_3 + AgO$.

CONSIDERATIONS ON THE FOREGOING FACTS.

Tannic and gallic acids, although of very different composition, yet yield the same products, only in different proportions, by the action of heat; namely, metagallic, pyrogallic, and carbonic acids, and water.

Tannic acid may be viewed as a compound of gallic and pyrogallic acids.



Now, since gallic acid contains the elements of carbonic and pyrogallic acids, or of carbonic acid, metagallic acid, and water, it is easy to see how all these products may be formed. The proportions, however, differ with the temperature. This renders it difficult to represent all the changes by one simple equation.

It is plain, however, that tannic, gallic, and pyrogallic acids, like the three acids described under meconic acid, have an intimate connexion. Further experiments must decide in what form the carbonic and pyrogallic acids exist in the tannic and gallic acids.

NUT-GALLS. ELLAGIC ACID.

From the puncture of an insect (*Cynips gallæ tinctoriæ* Olivier) there is produced, on the leaves of all species of quercus, the so-called Nut-galls. These, when of good quality, (Aleppo galls,) contain 30 to 50 per cent. of soluble matter, chiefly tannic acid.

The alcoholic or aqueous infusion of nut-galls is known by the name of tincture of galls. It contains variable proportions of tannic and gallic acids, and is used as a test.

It precipitates persalts of iron of a deep bluish-black colour; tin, yellowish; nickel, greenish-yellow; cobalt, whitish-yellow; cerium, yellow; copper, grey; titanate, red; tellurium, yellow; antimony, white; columbium, reddish-yellow; chromium, brown; molybdenum, brown; lead, white; uranium, reddish-brown; bismuth, reddish; silver, dirty yellow; platinum, dark green; gold, brown; osmium, violet.

A fresh infusion precipitates the salts of cinchonine, quinine, brucine, strychnia, codeine, narcotine, and morphia, all white. These precipitates are soluble in acetic acid.

When the infusion of nut-galls is exposed to the atmosphere, the tannic acid gradually disappears, and is replaced by gallic acid and an

insoluble grey powder. Chevreul found that this powder was soluble in alkalies, and precipitated by acids. He called it *Ellagic acid* (from *Galle* reversed). Braconnot observed, that it is formed in large quantity when nut-galls, moistened, are made to undergo fermentation. It forms with potash a crystallizable salt, insoluble in water, but soluble in alkalies. According to Pelouze, its formula is $C_7H_2O_4 + HO = C_7H_3O_5$, which is the composition of gallic acid dried at 212° . In the anhydrous state it has the same composition as the compound described by Robiquet as produced by the action of sulphuric acid on gallic acid; from which, however, it differs in its colour, and in the insolubility of its compound with potash.

Ellagic acid, when heated, yields a greenish-yellow vapour, which condenses into greenish-yellow crystals, which are soluble without change in sulphuric acid and alkalies, and are dissolved by nitric acid with a red colour, being converted into oxalic acid when the solution is heated for some time.

Grischon has found ellagic acid in the root of *Tormentilla officinalis*; and it has also been discovered by Taylor as the chief constituent of the bezoar stones, concretions formed in the intestines of certain herbivora. Mercklein and Wöhler have analyzed the acid of the bezoar, which they called bezoaric acid, and which they found identical with ellagic acid; but they give for both acids the formula $C_{14}H_2O_7, HO$, which is twice the formula of ellagic acid above given, minus 1 eq. of water. They also state, that by the action of the air on a solution of this acid in potash, there is formed a new acid, *Glaucomelanic acid*, $C_{12}H_2O_6, HO$, probably analogous in its origin to tannomelanic acid. It forms with potash a salt which separates in bluish-black crystals.

COMPOUNDS OF UNKNOWN CONSTITUTION SIMILAR IN THEIR RELATIONS TO TANNIC ACID.

Cinchona bark, catechu, and kino, the barks of the pine tribe, and many other vegetables, contain substances analogous to tannic acid, in so far as they are astringent, and are capable of combining with animal skin and gelatine. They differ from it, however, principally in causing a dark green or a grey precipitate with the persalts of iron, for which reason the name of *tannin which precipitates iron green*, and of *tannin which precipitates iron grey*, have been given to them collectively.

The experiments of Geiger, Berzelius, and Walzl tend to prove that the tannic acid in all plants is essentially the same; and that the green and grey colours of the precipitate with salts of iron are owing to the

presence of free acid; since the addition of a minute quantity of alkali changes these into the usual bluish-black caused by pure tannic or gallic acids.

CATECHU.

The substance known in commerce under the name of catechu is the dried watery extract of *Mimosa catechu*. (Willdenow.) It is astringent and bitter, with a sweetish after-taste. It contains a considerable quantity of tannic acid, soluble in cold water, and very similar in its properties to that of nut-galls. Hitherto, however, it has not been observed to yield when heated the same products as ordinary tannic acid. This modification of tannic acid requires a careful investigation.

CATECHINE.

The portion of catechu which is insoluble in cold water contains a peculiar principle, catechine or tanningenic acid, discovered by Büchner. It is soluble in hot water and in alcohol. The colouring matter dissolved along with it is removed by adding acetate of lead till the liquid becomes colourless, precipitating the lead by sulphate of soda, and allowing the clear liquor to cool, when the catechine is deposited. It can only be safely filtered through paper purified by hydrochloric acid from oxide of iron and lime, as it is coloured by contact with these bases.

Catechine forms a fine white powder composed of silky needles, fusible in a moderate heat, decomposed by a higher temperature. According to Büchner, if heated till it becomes brown, it is changed into tannic acid. It is very sparingly soluble in cold water. Its solution is coloured red by long exposure to the atmosphere, and, if now evaporated, leaves a red splintery mass, soluble in cold water. Catechine colours green the persalts of iron. It does not precipitate gelatine, tartar-emetic, or vegetable alkalies. According to Svanberg, its formula is $C_{15}H_6O_6$. This requires confirmation.

When exposed to the air in contact with caustic alkalies, it forms black solutions; with carbonated alkalies, red solutions. According to Svanberg, the former contain a new acid, *Japonic acid*, in combination with bases; the latter, another new acid, *Rubinic acid*.

Japonic acid, when separated from its salts, forms a black powder, soluble in hot water. Its formula is $C_{12}H_4O_4 + aq$. That of the japonate of silver is $C_{24}H_8O_8 + AgO$. (Svanberg.) According to this, 2 at. of acid lose 2 at. of water, which are replaced by 1 at. oxide of silver. This is rather improbable.

Rubinic acid has not been obtained in a separate form. Its formula, as it exists in the rubinate of silver, is $C_{18}H_6O_9$. (Svanberg.) The production of these compounds is not yet explained.

According to Pelouze, ether dissolves out of dry catechu a species of tannic acid, the formula of which is $C_{18}H_9O_8$. It remains to be determined whether this is catechine; from which, however, in the present state of our knowledge, it appears to differ in composition.

CITRIC ACID.

A tribasic acid. (Liebig.)

- A. Formula in the Salt of Silver . . . $C_{12}H_5O_{11} = \overline{Ci}$
 B. Formula of the Acid dried at 212° . . . $C_{12}H_5O_{11} + 3HO = \overline{Ci} + 3 \text{ aq.}$
 C. Formula of the Acid crystallized by cooling $C_{12}H_5O_{11} + 3HO + \text{aq.} = \overline{Ci} + 4 \text{ aq.}$
 D. Formula of the Acid formed at 61° . . . $C_{12}H_5O_{11} + 3HO + 2 \text{ aq.} = \overline{Ci} + 5 \text{ aq.}$

Discovered by Scheele in 1784. It is found in the juice of many fruits, particularly in those of the different species of *citrus*, *vaccinium*, and *ribes*.

To obtain it, citrate of lime is formed by adding chalk to lemon-juice; and this salt is afterwards decomposed by diluted sulphuric acid in slight excess, and the citric acid purified by crystallization. It is made in large quantity for the calico-printers and for medical purposes, and may be purchased at a cheap rate in a high degree of purity. It is chiefly used in medicine as an ingredient in effervescing powders.

It forms regular transparent crystals, very soluble, of a pleasant acid taste, which differ in the amount of water when formed at different temperatures, as in the above table. The acid D loses two atoms of water at 212° , and is converted into the acid B. The acid C does not lose water, even at 266° . All the modifications melt by heat; and if the heat be removed as soon as other products besides water appear, there is left a transparent deliquescent mass, which is a mixture of citric and aconitic acids. A higher temperature causes the production of carbonic oxide, carbonic acid, acetone, acetic acid, and two pyrogenous acids, with a trifling residue of carbon when the heat has been strong and rapidly applied.

By the action of oil of vitriol, aided by heat, citric acid is resolved into carbonic oxide, carbonic acid, acetic acid, and water, the elements of which it contains.

When melted with an excess of caustic potash, it is resolved into oxalic and acetic acids and water, which is merely a different arrangement of the same elements.

By oxidizing agents in general citric acid is partially converted into acetic acid.

When a few drops of a solution of citric acid are added to lime-water, a clear liquid results, which, when heated, deposits a white powder, soluble in acids without effervescence.

CITRATES.

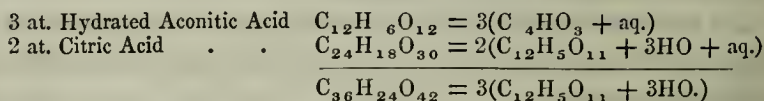
Citric acid forms with bases neutral and basic salts. These salts have recently been subjected to a most elaborate investigation by Heldt. The tribasic salts appear in two general forms, corresponding to the acids C and D. The former are $\overline{\text{Ci}}, 3\text{MO} + \text{aq}$, the latter are $\overline{\text{Ci}}, 3\text{MO} + 2\text{aq}$. The bibasic salts belong to the form $\overline{\text{Ci}} \left\{ \begin{smallmatrix} 2\text{MO} \\ \text{HO} \end{smallmatrix} \right\} + 2 \text{aq.}$, corresponding to the acid D. The monobasic salts also correspond to the acid D, being of the form $\overline{\text{Ci}} \left\{ \begin{smallmatrix} \text{MO} \\ 2\text{HO} \end{smallmatrix} \right\} + 2\text{aq.}$ In its relation to bases, the citric acid is strikingly analogous to tribasic phosphoric acid. When the tribasic citrates are heated, they lose their water of crystallization, and then correspond to the acid B.

In the basic salts, either the water of crystallization of the neutral salts is replaced by an equivalent of protoxide, $\overline{\text{Ci}} + 3\text{MO} + \text{MO}$, being thus also analogous to the acid C; or else, in addition to this, they contain 1 at. water of crystallization, $\overline{\text{Ci}} + 3\text{MO} + \left\{ \begin{smallmatrix} \text{MO} \\ \text{HO} \end{smallmatrix} \right\}$, in which case they correspond to the acid D.

The citrates of lead exhibit several forms of basic citrates, which are probably formed by the combination of the above-mentioned basic salts with one another, or with neutral citrates.

The citrates, when heated, froth, blacken, and give off an acid liquid.

When an anhydrous citrate, $\overline{\text{Ci}} + 3\text{MO}$, is decomposed by an alcoholic solution of hydrochloric acid, so that each equivalent of citric acid can only obtain 3 eq. water, formed by the oxygen of the oxide and the hydrogen of the hydrochloric acid, the citric acid resolves itself into hydrated aconitic acid, and the citric acid C; thus,



This is the same change which is produced by heat. (Berzelius.)

Citrate of Ammonia is a very soluble and crystallizable salt; the formula of which is $\overline{\text{Ci}} \left\{ \begin{smallmatrix} 2\text{NH}_4\text{O} \\ \text{HO} \end{smallmatrix} \right\}$.

Citrate of Oxide of Ethyle.—Formula, $\overline{\text{Ci}}, 3\text{AcO} + \text{aq.}$ (Heldt.) Discovered by Thenard. It is obtained by heating a mixture of citric acid, alcohol, and oil of vitriol, till ether begins to distil over. When the residue in the retort is mixed with water, the citric ether separates as a heavy oily fluid. It is washed with water, dissolved in alcohol, and decolorized by charcoal. The alcohol being dissipated by heat, leaves the new ether pure. It has a faint smell of olive oil, and a bitter taste. Sp. gr. = 1.142. It boils at 540° , but is partially decomposed, yielding carbon, pyrocitric acid, and alcohol. It is converted by alkalies into citric acid and alcohol; but is not altered by acids in the cold, nor by chlorine and bromine.

The monobasic and bibasic citrates of ethyle are not known. The citrates of methyle and glyceryle, &c. are also unknown.

Citrate of Potash.—Three citrates of potash exist, $\overline{\text{Ci}}, 3\text{KO}$; $\overline{\text{Ci}}, 2\text{KO}, \text{HO}$; and $\overline{\text{Ci}}, \text{KO}, 2\text{HO}$. They are soluble and crystallizable; and the first and third crystallize with 2 and 4 eq. of water of crystallization respectively.

Citrate of Soda.—Formula of the tribasic salt, $\overline{\text{Ci}}, 3\text{NaO}, 11\text{aq.}$ (Berzelius.) This salt forms large regular crystals. At 212° they lose 7 at. water, leaving $\overline{\text{Ci}}, 3\text{NaO}, 4\text{aq.}$ When heated to from 360° to 380° , the remaining 4 at. water are expelled; leaving the tribasic salt anhydrous.

The bibasic salt, $\overline{\text{Ci}}, 2\text{NaO}, \text{HO}, 2\text{aq.}$, is obtained by adding to a solution of the last salt half as much citric acid as it already contains. By spontaneous evaporation it forms small prismatic crystals.

The monobasic salt, $\overline{\text{Ci}}, \text{NaO}, 2\text{HO}, 2\text{aq.}$, is obtained by a similar process, adding a quantity of citric acid equal to that already present. It forms a gummy amorphous mass; but may be obtained in crystalline grains from an alcoholic solution.

Citrate of Baryta.—Two forms of this salt are known. Citrate of soda added to chloride of barium causes a white precipitate, $\overline{\text{Ci}}, 3\text{BaO}, 7\text{aq.}$ (Berzelius.) A heat of 300° expels 6 at., a higher temperature the last atom of water. When a hot solution of citric acid and chloride of barium is added to a hot solution of citrate of soda till the precipitate is dissolved, and the mixture allowed to cool, a crystalline powder is deposited, which contains $2\overline{\text{Ci}}, 5\text{BaO}, \text{HO} + 7\text{aq.}$ and must be viewed as a compound of the salt first described with a bibasic salt, $\overline{\text{Ci}}, 2\text{BaO}, \text{HO}$.

Citrate of Lime.—The tribasic salt, formed like that of baryta, is $\overline{\text{Ci}}, 3\text{CaO}, 4\text{aq.}$ (Berzelius.) The precipitate formed by heating citric

acid with an excess of lime-water is a bibasic salt. The salt formed by adding chalk to lemon or currant juice, from which citric acid is obtained, is a mixture of the two salts just described.

The citrates of magnesia, strontia, manganese, cobalt, and nickel are analogous to the foregoing. The citrates of zinc are analogous to those of baryta.

Citrate of Lead.—The tribasic salt, $\overline{\text{Ci}}, 3\text{PbO}, \text{aq.}$ is a white powder, resolved, by washing with water, into the soluble bibasic salt, and an insoluble salt with excess of base. The bibasic salt, $\overline{\text{Ci}}, 2\text{PbO}, \text{HO} + 2\text{aq.}$, forms crystalline grains. The basic citrate of lead occurs in two forms: the first is $\overline{\text{Ci}}, 6\text{PbO}, \text{aq.}$; the second $\overline{\text{Ci}}, 3\text{PbO} \left\{ \begin{smallmatrix} \text{PbO} \\ \text{HO} \end{smallmatrix} \right\}$. Another citrate of lead is $2\overline{\text{Ci}} \left\{ \begin{smallmatrix} 5\text{PbO} \\ \text{HO} \end{smallmatrix} \right\} + \text{aq.} = \overline{\text{Ci}}, 3\text{PbO} + \overline{\text{Ci}} \left\{ \begin{smallmatrix} 2\text{PbO} \\ \text{HO} \end{smallmatrix} \right\} + \text{aq.}$ Another is $\overline{\text{Ci}} \left\{ \begin{smallmatrix} 5\text{PbO} \\ \text{HO} \end{smallmatrix} \right\} + 2\text{aq.}$, which may be a compound of the two basic salts above mentioned; for the 2 eq. of water of crystallization being expelled by heat, there remains the dry salt $\overline{\text{Ci}} \left\{ \begin{smallmatrix} 5\text{PbO} \\ \text{HO} \end{smallmatrix} \right\}$, and this doubled is equal to $\overline{\text{Ci}} \left\{ \begin{smallmatrix} 6\text{PbO} \\ \text{HO} \end{smallmatrix} \right\} + \overline{\text{Ci}} \left\{ \begin{smallmatrix} 4\text{PbO} \\ \text{HO} \end{smallmatrix} \right\}$.

The only citrate of copper yet described is a green crystalline powder, $\overline{\text{Ci}}, 3\text{CuO}, \text{CuO}, \text{HO} = \overline{\text{Ci}}, 4\text{CuO}, \text{aq.}$ It contains, therefore, an excess of base.

Citrate of Silver forms a brilliant white powder, which, if washed and dried below 60° , is $\overline{\text{Ci}}, 3\text{AgO}, \text{aq.}$ When gently heated, it gives off water, and becomes $\overline{\text{Ci}}, 3\text{AgO}$.

Potash-citrate of Antimony.—This salt, which has properties analogous to tartar-emetic, forms dazzling white prisms. It is composed of $\overline{\text{Ci}}, \text{Sb}_2\text{O}_3 + \overline{\text{Ci}}, 3\text{KO} + 5\text{aq.}$ (Thaulow.) The water is expelled at 375° .

Like phosphoric acid, citric acid forms double salts with two bases, such as potash and soda, potash and ammonia, &c. The general characters of these salts correspond to those of the citrates above described.

ACTION OF HEAT ON CITRIC ACID.

This subject has occupied the attention of Lassaigne, Dumas, Baup, Robiquet, Dahlström, and Berzelius: but the products vary so much with the circumstances of the experiment, that their results appear contradictory and irreconcilable. The recent researches, however, of

Crasso (Liebig's Annalen, April 1840) have cleared up the whole subject, and reconciled the contradictions of his predecessors. We have only space for his results.

According to Crasso, then, crystallized citric acid, when exposed to heat, exhibits four stages of decomposition. During the first, the water of crystallization alone is given off, and the residue contains unaltered citric acid. The second stage is characterized by white vapours, and the production of acetone, carbonic oxide, and carbonic acid, while the residue consists of hydrated aconitic acid, which is therefore the true pyrocitric acid. In the third stage, the aconitic acid, not being volatile, is itself decomposed, yielding carbonic acid, and an oily liquid, which soon crystallizes. This is the pyroaconitic acid, the citric acid of Baup, for which Crasso proposes the name of Itaconic acid. In the fourth period, empyreumatic oil is produced, and a voluminous coal remains behind. Crasso has further shewn that the aconitic acid, heated by itself, is converted into itaconic acid and carbonic acid; and that the itaconic acid, when heated, yields a volatile acid isomeric with itself, which is identical with the citribic acid of Baup, which he proposes to call Citraconic acid, and which is always more or less formed along with the itaconic acid, owing to the easy decomposition of the latter. The action of heat on citric acid, therefore, gives rise to three distinct acids in regular sequence; 1st, aconitic or pyrocitric acid; 2nd, itaconic or pyroaconitic acid; 3rd, citraconic or pyro-itaconic acid.

ACONITIC ACID.

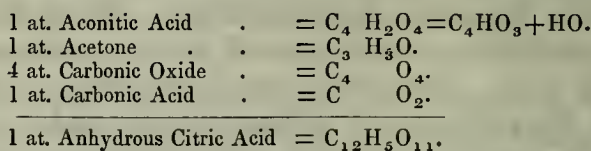
Formula, $C_4H_3O_3 + aq.$ Symb. $\overline{At} + aq.$

This acid was discovered by Peschier, in the *Aconitum napellus*, and analyzed by L. A. Büchner, jun. The acid observed by Braconot in *Equisetum fluviatile*, and analyzed by Regnault, seems to be identical with it; as does also the acid obtained from citric acid by Berzelius and Dahlström, as above described. It is easily extracted from the plants, by combining it with oxide of lead, decomposing the salt by sulphuretted hydrogen, and purifying the acid by solution in ether.

It forms a white crystalline mass, soluble in water, of a pleasant acid taste. It is decomposed by heat, yielding two new acids. Regnault supposed it to be identical with maleic acid; but, as the latter is converted by heat into fumaric acid, a change not observed in aconitic acid, this identity is doubtful. It ought to be mentioned also, that the acid from *Equisetum fluviatile* may be sublimed without change,

although in all other particulars identical with the acid from *Aconitum napellus*.

Its production is easily explained, for 1 at. anhydrous citric acid, $C_{12}H_5O_{11}$, yields



As above mentioned, this is the true pyrocitric acid.

ACONITATES.

The alkaline aconitates are soluble in water, the others insoluble or sparingly soluble. Their properties are not very interesting. The general formula for these salts is $\overline{At}, MO$. They sometimes contain water of crystallization.

There is some reason to believe that this acid may prove to be tri-basic. It will then have the formula $C_{12}H_3O_9 + 3HO$; and the neutral aconitates will have the formula $C_{12}H_3O_9 + 3Mo$. Future investigations must determine this point.

ITACONIC ACID.

Syn. Pyrocitric Acid; Citricic Acid. (Baup.)—Formula, $C_5H_2O_3 + HO$. Symb. $\overline{It} + aq$.

This acid is obtained, as above mentioned, in the third stage of the distillation of citric acid, or by the action of heat on aconitic acid. It is generally accompanied by some of the acid next to be described, citraconic acid. It may be obtained from the oily mass which distils over, and which commonly crystallizes after a short time, by solution in absolute alcohol, and spontaneous evaporation. The crystals thus obtained, when dissolved in water, yield by slow evaporation large rhomboidal crystals, or octahedrons, soluble in 17 parts of water at 60° .

There is some reason to suppose that it may be a bibasic acid, in which case its formula will be $C_{10}H_4O_6 + 2HO$. In the production of this acid from aconitic acid, 3 at. hydrated aconitic acid, $3(C_4HO_3 + HO) = C_{12}H_6O_{12}$, yield 2 at. carbonic acid, $2CO_2$, and 2 at. itaconic acid, $2(C_5H_2O_3 + HO)$.

ITACONATES.

The neutral itaconates have the general formula $C_5H_2O_3 + MO$, or $C_{10}H_4O_6 + 2MO$. The acid salts are either $2(C_5H_2O_3) + MO + HO$, or $C_{10}H_4O_6 + \left\{ \begin{smallmatrix} MO \\ HO \end{smallmatrix} \right\}$. They have been studied by Baup and Crasso, to whose memoirs the reader is referred for details.

CITRACONIC ACID.

Syn. Pyrocitric Acid; Citribic Acid. (Baup.)—Formula, $C_5H_2O_3 + HO$. Symb. Ct + aq.

This acid is formed by the action of heat on itaconic acid, with which it is isomeric. It is volatile, and thus escapes the further action of the heat. It is soluble in less than half its weight of water at 60° , and very soluble in alcohol and ether. It is very probably also a bibasic acid, having the formula $C_{10}H_4O_6 + 2HO$; but this must be determined by future researches.

CITRACONATES.

Citraconic acid forms neutral and acid salts, which have been examined by Crasso. The neutral salts have the general formula $C_5H_2O_3 + MO$, or $C_{10}H_4O_6 + 2MO$. The acid salts are either $2(C_5H_2O_3) + HO + MO$, or $C_{10}H_4O_6 + \left\{ \begin{smallmatrix} HO \\ MO \end{smallmatrix} \right\}$. It forms with ammoniacal gas a peculiar amorphous compound, which does not contain the water usually present in ammoniacal salts. The formula of this compound is $2(C_5H_2O_3) + NH_3$. When this substance is dissolved in water, and the solution evaporated, it yields crystals of the acid citraconate of ammonia, $2(C_5H_2O_3) + NH_2O + HO$. (Crasso.)

TARTARIC ACID.

A bibasic acid. Formula of the crystallized acid, $C_8H_4O_{10} + 2 \text{ aq.}$; of the acid in the bibasic salts, $C_8H_4O_{10} = \overline{T}$. When tartar-emetic dried at 212° is exposed to a stronger heat, it loses water, and there remains in the salt an acid, the formula of which must be $C_8H_2O_8$; but when this salt is re-dissolved in water, the original acid is re-produced. (Liebig.)

Tartaric acid occurs chiefly in the juice of the grape, but also in

many other fruits and parts of vegetables. It was discovered by Scheele in 1770. It is extracted from the tartar of the grape, which is monobasic tartrate of potash, $\overline{T}, KO, HO$, by a process similar to that employed for citric acid, namely, converting it into tartrate of lime, and decomposing this salt by sulphuric acid. It is prepared in large quantity for the calico-printers and for medical use, and is sold in a state of purity at a very low price. Its medical use is the same as that of citric acid. It cannot be easily prepared in the laboratory on a small scale; but a process is given in the Pharmacopœia for making it. Tartaric acid forms large transparent, oblique, rhombic prisms, which have a pleasant sour taste. The aqueous solution becomes mouldy by keeping: the solution in alcohol, when heated, is converted into monobasic tartrate of oxide of ethyle. When heated it melts, and yields a variety of new and interesting products.

It contains the elements of 1 at. hydrated acetic acid, and 2 at. hydrated oxalic acid; or of 2 at. hydrated formic acid, and 1 at. anhydrous malic acid. When heated with caustic alkalies, it is resolved into acetic and oxalic acids. (Gay-Lussac.) With hyperoxides it yields formic acid, carbonic acid, and tartrate of protoxide: with diluted sulphuric acid it yields a large quantity of formic acid.

A solution of tartaric acid causes, with solutions of caustic lime, baryta, and strontia, white precipitates soluble in excess of acid. It does not precipitate the salts of these earths. It is used as a test for potash and its salts, in which it produces the sparingly soluble monobasic tartrate of potash (cream of tartar). The presence of tartaric acid in the solutions of many metallic oxides prevents their precipitation by alkalies.

TARTRATES.

Tartaric acid forms with bases monobasic and bibasic salts. The former are acid, and have the formula $\overline{T}, MO, HO$: the latter are neutral, and their formula is $\overline{T}, 2MO$. These 2 eq. of metallic oxides may be different: hence a series of salts with two bases, $T \left\{ \begin{array}{l} MO \\ mO \end{array} \right\}$.

With potash and oxide of antimony, tartaric acid forms an important series of compounds. Tartar-emetic contains, for 1 eq. tartaric acid, 1 at. = 3 eq. teroxide of antimony, and 1 eq. of potash; it must therefore be viewed as a salt with excess of base. The neutral salt has been lately described. As already mentioned, tartar-emetic at 392° , without blackening, gives off 2 at. water, formed either at the expense of the acid, or by part of the oxygen of the teroxide, with hydrogen from the acid. In the latter case it must contain either metallic anti-

mony or a protoxide; but, at all events, it no longer belongs, in this state, to the regular series of the tartrates. When put into water, however, tartar-emetic is re-produced. (Liebig.) At 570° all the tartrates are blackened, and yield a peculiar smell, which is characteristic of this family of salts.

The soluble neutral tartrates become insoluble or sparingly soluble by the addition of tartaric acid; the insoluble or sparingly soluble are rendered soluble by such addition. The tartrates insoluble in water are distinguished by their easy and complete solubility in caustic potash or ammonia.

The tartrates are among the most interesting of organic salts. Our knowledge of them, however, is very far from complete, and a careful study of them will certainly lead to very important results in regard to the true theory of all such combinations.

Tartrate of Ammonia.—*a.* Neutral or bibasic. $\bar{T}, 2AdH_2O + 2aq.$ (Dulk.) This salt is crystallizable. Its solution, when evaporated, loses ammonia and yields the acid salt. *b.* Acid or monobasic. $\bar{T}, AdH_2O, aq.$ (Dulk.) This is a crystalline powder, very soluble in hot, sparingly soluble in cold water. It corresponds to cream of tartar.

Tartrate of Oxide of Ethyle.—The neutral or bibasic salt is not yet known. The acid salt, $\bar{T}, AeO, aq.$ (Guérin Varry), is produced by heating tartaric acid with alcohol; and may be obtained pure by decomposing the double tartrate of baryta and ethyle with sulphuric acid, and evaporating the filtered solution in vacuo. It crystallizes in elongated rhombic prisms, and is very soluble in water and alcohol, insoluble in ether. It is decomposed by heat, with the usual smell of the tartrates. This compound was formerly called tartrovinic acid; it forms with bases double salts, formerly called tartrovinates. It dissolves zinc and iron with disengagement of hydrogen.

Tartrate of Ammonia and Ethyle.— $\bar{T}, AeO, AdH_2O.$ —This salt forms a shining, silky, crystalline and fibrous mass. (Guérin Varry.)

Tartrate of Oxide of Methyle.—The acid salt, $\bar{T}, MeO, aq.,$ is formed in the same way as the tartrovinic acid. It crystallizes in fine needles, and forms a series of double salts. (Guérin Varry.)

Tartrate of Potash. *Syn. Tartar; Cream of Tartar; Bitartrate of Potash.*—*a.* Acid or monobasic. Formula, $\bar{T}, KO, HO.$ —This important salt occurs in many vegetable juices, but in largest quantity in the juice of the grape; from which it separates in a more or less coloured crystalline crust, as soon as the sugar by fermentation has been converted into alcohol, in which it is insoluble. It is purified by re-

crystallization, when it forms, on cooling, a crust on the surface of the liquid: hence the name *Cremor tartari*.

It forms hard, opaque, oblique, rhombic prisms, or irregular six-sided prisms. It feels gritty between the teeth, has a faint acid taste, and is permanent in the air. When heated, it melts, froths, gives out the peculiar smell of the heated tartrates, and yields by distillation a solid acid, one of the pyrogenous tartaric acids. It is soluble in 18 parts of boiling water, and in 184 parts at 70°. From its insolubility, it is always formed when an excess of tartaric acid is brought into contact with a salt of potash. Stirring with a glass rod, and the addition of alcohol, hasten its separation. Potash may thus be detected and distinguished from soda.

The purest carbonate of potash (salt of tartar) is obtained by igniting cream of tartar. The residue is the well-known *black flux*, a mixture of charcoal with carbonate of potash; from which water dissolves the carbonate. If made with raw tartar, which contains nitrogen, it is contaminated by cyanide of potassium. When 2 parts of nitre and 1 of tartar are ignited, *white flux* is left, which is nothing else than carbonate of potash, all the charcoal having been oxidized by the nitric acid. Tartar always contains a little tartrate of lime.

Cream of tartar is much used in dyeing, from its power of dissolving metallic oxides. In medicine it is very often used as a laxative and diuretic, and to form an acidulous drink in febrile diseases.

b. Neutral or bibasic.—This salt, the soluble tartar of the pharmacopœia, $\overline{\text{T}}, 2\text{KO}$, is easily obtained by adding cream of tartar to a hot solution of carbonate of potash till all effervescence ceases, and the liquid is quite neutral. It forms transparent right rhombic prisms, and has a mild saline, somewhat bitter taste. It is used as a laxative.

Tartrate of Potash and Ammonia. Syn. Ammoniated Tartar.—Formula, $\overline{\text{T}}, \text{KO}, \text{AdH}_2\text{O} + \text{aq}$. It is formed by neutralizing cream of tartar with ammonia, and crystallizing the solution. It forms right rhombic prisms, large and transparent; and has a cooling, pungent, saline taste. It is very soluble in water; and the solution, when heated, loses ammonia, and deposits cream of tartar. It is decomposed by acids in the same way, tartar being deposited. This salt is used in medicine as a laxative, especially on the Continent.

Tartrate of Potash and Ethyle.— $\overline{\text{T}}, \text{KO}, \text{AeO} + \text{aq}$. (Guérin Varry.) Obtained by adding a slight excess of sulphate of potash to the double salt of baryta and ethyle, and evaporating the filtered solution. It crystallizes in the same form as the preceding salt, being isomorphous

with it. Its solution, when heated, is resolved into cream of tartar and alcohol. Guérin Varry mentions another compound of the same ingredients, which has an alkaline reaction, and crystallizes in eight-sided prisms. Its composition is unknown.

Tartrate of Potash and Methyle.— $\overline{T}, KO, MeO + aq.$ (Guérin Varry.) A crystallizable salt, analogous in its mode of formation and in its properties to the foregoing.

Tartrate of Potash and Boracic Acid. *Syn. Soluble Tartar of the French Pharmacopœia.*— $\overline{T}, KO, BO_3.$ (Duflos.) Cream of tartar and boracic acid, in the proportion of their equivalents, are kept in contact with warm water till all is dissolved, and the liquid then evaporated to dryness. It forms a white amorphous mass, of a sour taste, very soluble in water, insoluble in alcohol. Soubeiran recommends 4 parts of tartar to 1 of boracic acid, which yields $3\overline{T} + 3KO + BO_3.$ The salt of Duflos is exactly analogous to tartar-emetic; that of Soubeiran to the neutral tartrate of potash and antimony lately discovered. The first salt dissolves a large quantity of cream of tartar, which by evaporation it deposits in crystals. (Duflos.) The solution must not be boiled, otherwise some boracic acid is dissipated. This compound is used as a laxative on the Continent.

Tartrate of Potash and Arsenious Acid.—According to Mitscherlich, this compound may be formed, and is analogous in form and composition to tartar-emetic. Probable formula, $\overline{T}, KO, AsO_3.$ The mode of preparing it has not been described.

Tartrate of Soda.—*a.* Acid or monobasic: $\overline{T}, NaO, HO + 2 aq.$ (Bucholz.) Formed by adding tartaric acid to the neutral salt. Six-sided prisms, very sour to the taste, very soluble in water. It is used to prepare chlorate of soda from chlorate of potash. When mixed with the latter, eq. to eq., cream of tartar and chlorate of soda are produced.—*b.* Neutral or bibasic: $\overline{T}, 2NaO + 4 aq.$ Formed by neutralizing tartaric acid with soda. Transparent prisms, permanent in the air, very soluble.

Seidlitz Powders, or Carbonated Effervescing Cheltenham Salts, are an intimate mixture of equal parts of tartaric acid and bicarbonate of soda in atomic proportions. To these is often added a portion of sulphate of magnesia, or of the tartrate of potash and soda (Rochelle salt). The powders must be well dried; otherwise they slowly act on each other, and lose the effervescing quality.

Tartrate of Soda and Ethyle.— $\overline{T}, NaO, AcO, 2 aq.$ (Guérin Varry.) White rhomboidal tables.

Tartrate of Potash and Soda. *Syn. Rochelle Salt; Salt of*

Seignette.— $\overline{T}, KO, NaO + 10aq.$ (Schulze.) Formed by neutralizing carbonate of soda with cream of tartar. It forms very large transparent right rhombic, or six, eight, and ten-sided prisms. It has a very mild, hardly saline taste; and may be given in soup or beef-tea in a sufficient dose, without the knowledge of the patient, from its comparative tastelessness. It acts as a laxative, like neutral salts in general.

This salt forms with the tartrate of potash and boracic acid of Duflos a double salt ($\overline{T}, KO, NaO$) + ($\overline{T}, KO, BO_3$). (Duflos.) *Syn. Boracic Tartar; Tartarized Borax*. One part of borax (biborate of soda) and 3 of cream of tartar are dissolved in 20 of water. The clear portion is evaporated to dryness, and yields a gummy mass, of an acidulous saline taste, deliquescent in the air. The powder, if not very long and carefully dried, and stirred in the drying, has the inconvenience of caking in the bottles in which it is kept, so that it cannot be extracted without breaking them. It is much used in medicine on the Continent.

Tartrate of Lithia.—*a.* Monobasic: $\overline{T}, LO, HO + 3aq.$ (Dulk.)
b. Bibasic: $\overline{T}, 2LO.$ (Dulk.) The former is crystallizable and very soluble; the latter forms a crystalline mass. Tartrate of lithia and potash, $\overline{T}, KO, LO + 2aq.$, and of lithia and soda, $\overline{T}, NaO, LO + 4aq.$, are both soluble and crystallizable. (Dulk.)

Tartrate of Baryta.— $\overline{T}, 2BaO + 2aq.$ (Dulk.) A white powder, insoluble in water, soluble in tartaric acid.

Tartrate of Baryta and Ethyle.— $\overline{T}, BaO, AeO + 2aq.$ (Guérin Varry.) A solution of tartaric acid in alcohol is first heated, then mixed with water, and neutralized with carbonate of baryta. The filtered liquid yields, by spontaneous evaporation, crystals of this salt, which are soluble in water.

Tartrate of Baryta and Methyle.— $\overline{T}, BaO, MeO + aq.$ (Dumas and Péligot.) Analogous to the foregoing salt. It is very soluble in water and crystallizable.

Tartrate of Baryta and Potash, $\overline{T}, BaO, KO + 2aq.$, and *Tartrate of Baryta and Soda*, $\overline{T}, BaO, NaO + 2aq.$, are both sparingly soluble crystalline powders. (Dulk.)

Tartrate of Strontia.— $\overline{T}, 2SrO + 8aq.$ (Dulk.) Small four-sided tabular crystals, which lose all their water by a gentle heat or in vacuo.

With strontia tartaric acid forms a series of double salts, analogous to those above described with baryta.

Tartrate of Lime.— $\overline{T}, 2CaO.$ This salt, which is formed by neu-

tralizing with the atomic proportion of chalk a boiling solution of cream of tartar, is a white insoluble powder. The filtered liquid, which contains half the tartaric acid in the form of neutral tartrate of potash, yields a quantity of tartrate of lime equal to the first, by the addition of an atom of chloride of calcium. It is from this salt that all the tartaric acid of commerce is obtained, as formerly mentioned.

Of the remaining tartrates the most important are those of antimony and potash and of iron and potash, both of which are used in medicine. These will be described; but, in regard to the numerous tartrates and double tartrates which might be enumerated, the salts already described will give a sufficiently clear idea of their constitution, while we cannot here afford space for a detailed account of them.

Tartrate of Potash and Teroxide of Antimony. Syn. Tartar-Emetic; Tartarized Antimony.—*a.* With excess of base.—Formula, $\overline{\text{T}}, \text{KO}, \text{SbO}_3 + 2\text{aq.}$ This very important compound is prepared by boiling cream of tartar and finely powdered teroxide of antimony, in atomic proportions, with water, till all is dissolved. The solution, when evaporated, deposits octohedral crystals of tartar-emetic. Minute directions for its preparation are given in the Pharmacopœiæ and Dispensatories. Its uses in medicine as an emetic, purgative, diaphoretic, sedative, febrifuge, and counter-irritant, are so well known and important, that it may be truly said that no mineral remedy, except perhaps calomel, is more useful to the practitioner.

When heated to 212° , the crystals become anhydrous. Their formula then is $\text{C}_8\text{H}_4\text{O}_{10}, \text{KO}, \text{SbO}_3$. But when heated to 480° , they give off, as already mentioned, 2 at. of water, the elements of which must be derived either from the acid alone, or from the sesquioxide and acid together. Their formula then is $\text{C}_8\text{H}_2\text{O}_8, \text{KO}, \text{SbO}_3$, or $\text{C}_8\text{H}_2\text{O}_{10}, \text{KO}, \text{SbO}$; or they may contain antimony in the metallic state. It might be supposed that tartaric acid, as it exists in tartrate of silver and tartar-emetic at 212° , $\text{C}_8\text{H}_4\text{O}_{10}$, contains 2 at. of water ready formed, and that the anhydrous acid is really $\text{C}_8\text{H}_2\text{O}_8$. In favour of this view might be adduced the fact that tartar-emetic, heated to 480° , when dissolved in water, is restored to its original composition. But not only is it contrary to all analogy to suppose the existence of water ready formed in a salt of silver heated to 212° , such salts being without exception anhydrous; but, moreover, this assumption would lead to many other most improbable conclusions. For the present, therefore, we must consider the tartaric acid, anhydrous, to be $\text{C}_8\text{H}_4\text{O}_{10}$; and we must ascribe the appearance of the 2 at. of water when dry tartar-emetic is heated to 480° , to a partial reduction of the oxide of antimony by the hydrogen of the acid. Liebig considers that a part

of the antimony is actually reduced to the metallic state; as above explained, it seems to me possible that a protoxide may be formed, SbO , which must then be combined with an acid, the formula of which will be $\text{C}_8\text{H}_2\text{O}_{10}$. Such a protoxide of antimony, however, is unknown. In every view the change produced on tartar-emetic at 480° is most interesting. It occurs in no other salt save tartar-emetic, and hence must be owing to the presence in that salt of an oxide containing 2 at. oxygen more than the usual bases (protoxides). Possibly the same change may occur in the compounds of cream of tartar with boracic acid, arsenious acid, and peroxide of iron; all of which, like teroxide of antimony, contain 3 at. oxygen. For a full discussion of this subject I refer to Liebig's paper. (Ann. der Pharm. xxvi. 113.)

b. Neutral Tartrate of Antimony and Potash.—This salt, $3\bar{\text{T}}, 3\text{KO}, \text{SbO}_3$, is found in the mother-liquid of the crystallization of tartar-emetic, especially where an excess of cream of tartar has been used. It forms small crystals grouped together, but crystallizes with difficulty. By boiling its solution with teroxide of antimony, it may be entirely crystallized as tartar-emetic. Hence the importance of having a slight excess of oxide of antimony in the preparation of tartar-emetic. Other salts of tartaric acid, antimony, and potash are found in the same mother-liquid, the nature of which is not yet sufficiently known.

Tartrate of Potash and Sesquioxide of Iron. Syn. Tartarized Iron.—This salt is formed, according to the Pharmacopœiæ, by exposing for a long time to the air a mixture of cream of tartar and iron filings moistened with water. A soluble brown compound is gradually formed, the iron absorbing oxygen from the atmosphere. The solution, when evaporated, leaves an amorphous gummy mass, which dissolves readily in water. It might probably be easily formed by digesting cream of tartar with hydrated peroxide of iron. Its probable formula is $\bar{\text{T}}, \text{KO}, \text{Fe}_2\text{O}_3$: but a neutral compound probably exists, $3\bar{\text{T}}, 3\text{KO}, \text{Fe}_2\text{O}_3$. The tartarized iron is used in medicine.

Tartrate of Lead.—A white insoluble powder, which, when heated in close vessels, leaves a mixture of carbon and metallic lead in a state of minute division, which takes fire spontaneously when exposed to the air. Formula, $\bar{\text{T}}, 2\text{PbO}$.

Tartrate of Silver.— $\bar{\text{T}}, 2\text{AgO}$. This salt is soluble in hot water, and on cooling crystallizes in silvery scales.

ACTION OF HEAT ON TARTARIC ACID.

This subject has been most ably and minutely investigated by Fremy. (Ann. der Pharm. xxix. 142.) When tartaric acid is heated, with certain precautions, it melts, and gives off one-fourth of its water. It is now deliquescent, and forms soluble salts with lime and baryta, by which means it may be purified from tartaric acid. This new acid, to which Fremy has given the name of *Tartralic acid*, has in its salts the same composition as tartaric acid, but neutralizes one-fourth less base. It differs from tartaric acid, therefore, as pyrophosphoric acid differs from phosphoric acid. The general formula of its salts is, $C_8H_4O_{10} + 1\frac{1}{2}MO$; or, more correctly, $C_{16}H_8O_{20} + 3MO$.

Tartrate of Lime.— $C_{16}H_8O_{20}, 3CaO + 3aq$. The solution of this salt undergoes spontaneous decomposition, yielding tartrate of lime and free tartaric acid. Thus, 2 at. tartrate of lime, $2(C_{16}H_8O_{20}, 3CaO + 3aq)$, yield 3 at. tartrate of lime, $3(C_8H_4O_{10}, 2CaO + 2aq)$ and 1 at. tartaric acid, $C_8H_4O_{10}$, which takes up 2 at. water from the liquid.

The tartrate of baryta is analogous to that of lime. Tartrate of lead is anhydrous, $C_{16}H_8O_{20}, 3PbO$.

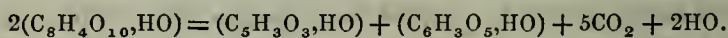
When tartralic acid is still further heated, it loses more water, and is converted into tartrelic acid, $C_8H_4O_{10} + HO$: this is still the composition of tartaric acid, but with only half the neutralizing power. It corresponds to metaphosphoric acid. Its salts have the general formula, $C_8H_4O_{10}, MO$.

The tartrelates of lead, baryta, and lime are anhydrous. In contact with water, the tartrelic acid, as well as the tartralic, passes into tartaric acid, just as happens with the modified phosphoric acids. The tartrelates also, in contact with water, yield tartrates and free tartaric acid; for 2 at. tartrelate of a protoxide, $2(C_8H_4O_{10}, MO)$, give 1 at. tartrate $C_8H_4O_{10}, 2MO$, and 1 at. tartaric acid $C_8H_4O_{10}$, which take 2 at. water from the liquid.

When the heat is raised still further, tartaric, tartralic, and tartrelic acids all lose the whole of their water, and leave anhydrous tartaric acid, $C_8H_4O_{10}$. This is the first instance of an organic acid in the anhydrous state; but it has lost all acid properties, and is quite insoluble in water. This is a powerful argument in favour of the view, according to which all acids are compounds of hydrogen. This inert, insoluble, anhydrous tartaric acid, when left long in contact with water, takes up the elements of that fluid by degrees, and passes through the stages of tartrelic and tartralic acids into tartaric acid. According to

the hypothesis just alluded to, tartrelic acid will be $C_8H_4O_{11} + H$; tartralic acid, $C_{16}H_8O_{23} + H_3$; and tartaric acid, $C_8H_4O_{12} + H_2$.

By a still higher temperature tartaric acid is decomposed, yielding carbonic acid, water, and two pyrogenous acids, one of which is crystalline, the other oily. The crystalline acid is $C_5H_3O_3 + aq.$ (Pelouze); the oily acid is $C_6H_3O_5 + aq.$ (Berzelius). They are formed from 2 at. tartrelic acid, according to the following equation:—



For details concerning these acids, I must refer to the original memoirs in the foreign journals.

RACEMIC ACID.

Syn. Paratartaric Acid; Acid of the Vosges.—Formula, $C_8H_4O_{10} + 2HO$. Symb. $\bar{R}$. This remarkable acid, which, in its parallelism with tartaric acid, affords the most complete and curious example of isomerism, is found in the juice of the grape, particularly in the district of the Vosges, replacing the ordinary tartaric acid. Its composition, as far as our present knowledge extends, is not only the same in 100 parts as that of tartaric acid; but its atomic weight, derived from the analyses of its salts, appears to be exactly the same. Moreover, its salts, although quite distinct from those of tartaric acid, are singularly analogous to them. It cannot be doubted, however, that there must be a real difference in the constitution of these acids, and that this will be discovered as soon as the salts of both acids have been submitted to a minute and thorough investigation. There is nothing yet known, for example, inconsistent with the supposition that racemic acid may be an acid requiring 4 atoms of base to form neutral salts, in which case its formula would be $C_{16}H_8O_{20} + 4HO$.

The crystallized racemic acid contains more water than crystallized tartaric acid. Its formula is $C_8H_4O_{10}, 2HO + 2aq.$ The two atoms of water of crystallization are expelled by a heat of about 300° , and the remaining acid has the composition of crystallized tartaric acid. It might be supposed to be anhydrous, and therefore to differ in composition from tartaric acid, were it not that, in combining with bases, with oxide of silver for example, it loses the two atoms of water remaining, which are replaced by metallic oxide.

The action of heat on racemic acid has been studied by Fremy and Berzelius. The former has shewn that it yields three compounds, corresponding to those from tartaric acid, and quite analogous to them. These he calls paratartralic, paratartrelic, and anhydrous racemic acid; the composition of which is the same as that of the corresponding pro-

ducts from tartaric acid. Berzelius has found that racemic acid, when distilled, yields the same products as tartaric acid, namely, carbonic acid, water, and the two pyrotartaric acids formerly described.

With potash and teroxide of antimony, racemic acid yields a tartar-emetic, distinct in properties from that made with tartaric acid, but identical with it in composition: $\overline{R}, K\overline{O}, Sb_2O_3$. This salt, when heated to 480° or 500° , undergoes the same curious change as tartar-emetic, giving off 2 at. of water.

The action of racemic acid on alcohol corresponds to that of tartaric acid; and in general its tendency to form salts with two different bases is the same as that of tartaric acid.

These two acids are distinguished by the more sparing solubility of racemic acid, by the force with which it retains its combined water, and by the crystalline form of their salts, which frequently differ in the amount of water of crystallization. The racemates have recently been very minutely studied by Fresenius, who has not, however, been able to establish the true nature of the difference between racemic and tartaric acids. At first, he could not obtain a double racemate of potash and soda, and was inclined to regard racemic acid as monobasic, $C_4H_2O_5, HO$. But that salt has since been obtained, and to all appearance the bibasic character of racemic acid is as well marked as that of tartaric acid. There must be a difference in the constitution of the two acids, but as yet we have no idea what that difference will prove to be.

MALIC ACID.

Formula, $C_5H_4O_8 + 2HO$. (Liebig.) Symb. $\overline{M}$. A bibasic acid. This acid is found in many fruits, particularly in the apple. It is most easily obtained from the fruit of *Sorbus aucuparia* (mountain ash or rowan tree) immediately after it has turned red, but while still unripe. The juice is heated to coagulate some albuminous matter, and filtered. It is then nearly neutralized with ammonia, and to 72 parts of juice a solution of 1 part of acetate of lead is added. This causes a precipitate of tartrate and citrate of lead. The filtered liquid is now precipitated by nitrate of lead, and the precipitate allowed to stand in the liquid till it has changed into a mass of crystals. This is well washed, dried, powdered, suspended in water, and decomposed by a current of sulphuretted hydrogen. The filtered liquid is neutralized with ammonia, and decolorized by digestion with animal charcoal. The colourless malate of ammonia is again precipitated by nitrate of lead, and the malate of lead decomposed by sulphuretted hydrogen. By this process Winkler obtained from 296 ounces of juice 19 ounces of pure

malate of lead, or upwards of 6 ounces of crystallized malic acid. Liebig recommends converting the first impure solution of the acid into acid malate of ammonia by neutralizing one half, and mixing it with the other. This salt forms large crystals, and is easily obtained colourless. Another process is to convert the impure malic acid into bibasic malate of lime, and to dissolve that salt in warm dilute nitric acid; when on cooling the acid or monobasic malate of lime is deposited in crystals, nearly pure, which are easily purified by re-crystallization. From that salt the acid may be extracted in the usual way.

Malic acid is exceedingly soluble in water, and crystallizes with more difficulty than the foregoing acids. It has a very pleasant acid taste. When exposed to heat, it yields two pyrogenous acids, called by Pelouze, who examined them, malic and paramaleic acids. They are isomeric, and appear to be identical with two acids found in the vegetable kingdom, namely, equisetie (aconitic?) acid and fumaric acid.

MALATES.

Malic acid, like tartaric acid, forms neutral or bibasic salts, acid or monobasic salts, and a third class, which are neutral and bibasic, but contain two different bases.

Malate of Ammonia.—The acid or monobasic salt has been described by Liebig. It forms large transparent crystals, resembling white sugar-candy. It is used in the preparation of pure malic acid and malates. Formula, $\overline{M}, \text{AdH}_2\text{O}, \text{HO}$.

Malate of Lime.—*a.* Bibasic. This salt is formed when malic acid is neutralized by lime water. It is soluble in water when formed, and continues so if dried at the ordinary temperature. Formula, $\overline{M}, 2\text{CaO} + 2\text{aq}$. If its solution be boiled, the salt loses 1 at. of water, and becomes $\overline{M}, 2\text{CaO} + \text{aq}$, which is an insoluble salt. The last atom of water is expelled by a heat of nearly 400° , and the anhydrous salt is left, $\overline{M}, 2\text{CaO}$. (Richardson and Merzdorf).—*b.* Monobasic. This salt is obtained by digesting, in the cold, malic acid with chalk, and gently evaporating the solution, when the acid malate crystallizes; or by dissolving the preceding salt with the aid of heat in dilute nitric acid, when the acid salt crystallizes on cooling. When heated to 390° , it is $\overline{M}, \text{CaO}, \text{HO}$. If heated only to 212° , it is $\overline{M}, \text{CaO}, \text{HO} + 4\text{aq}$. If dried at the ordinary temperature, $\overline{M}, \text{CaO}, \text{HO} + 8\text{aq}$.

Malate of Baryta.—When a solution of carbonate of baryta is evaporated in vacuo, it yields soluble crystals which are hydrated

bibasic malate of baryta, $\overline{M}, 2BaO + 2aq.$ If evaporated at a higher temperature, it deposits a crystalline powder, almost insoluble, which is the anhydrous salt, $\overline{M}, 2BaO.$

Malate of Lead.—The malic acid has a great tendency to form with lead the monobasic or acid salt. This was first obtained by Donovan, who thought that it contained a new acid, sorbic acid. It forms shining silvery scales. Formula, $\overline{M}, PbO, HO.$

Malate of Copper.—According to Richardson and Merzdorf, this salt is a bibasic salt with excess of base. It occurs in three forms: $\overline{M}, 2CuO, CuO + 6aq.;$ $\overline{M}, 2CuO, CuO + 5aq.;$ and $\overline{M}, 2CuO, CuO + 4aq.$ The two former are soluble in water: when their solutions are heated, the latter salt is deposited, which is insoluble.

The malates in general are little known, and require a minute investigation. The composition of the malate of copper differs remarkably from that of the other salts, and renders it probable that the true constitution of malic acid is yet unknown.

ACTION OF HEAT ON MALIC ACID.

When crystallized malic acid is kept for a long time at a temperature a little higher than its melting point, it loses water, and is entirely converted into fumaric or paramaleic acid. But if it be distilled by a very quick fire, it yields a volatile product, which is equisetie or maleic acid, while fumaric acid remains in the retort. These two acids have different properties, but the same composition in 100 parts; but they differ in atomic weight, one being bibasic, and the other monobasic.

MALEIC ACID.

A bibasic acid. Formula, $C_8H_2O_6 + 2HO.$ Symb. $\overline{Ma}.$ When malic acid is distilled with a quick fire, maleic acid passes over with water, in which it is dissolved, and from which it is separated in crystals by evaporation. The crystals are plates, or oblique rhombic prisms, very soluble in water, alcohol, and ether. These solutions have a taste at first sour, afterwards nauseous and metallic. It is distinguished from aconitic acid, which has the same composition; by the action of heat, which resolves it into water and anhydrous maleic acid. If kept for a long time melted at a lower temperature, it gradually passes, like malic acid, into a crystalline mass of fumaric acid. Maleic acid differs from malic acid in containing 2 at. of water less, which sufficiently explains its formation. It was formerly supposed to be

identical with equisetetic or aconitic acid; but, from the recent researches of Liebig, maleic acid appears to be decidedly bibasic.

The salts of maleic acid are insoluble, or sparingly soluble. The maleate of lead is $\overline{\text{Ma}}, 2\text{PbO} + 6\text{aq.}$ (Pelouze.) There are two maleates of silver: neutral and acid. The former is $\overline{\text{Ma}}, 2\text{AgO}$; the latter $\overline{\text{Ma}}. \left\{ \begin{array}{c} \text{AgO} \\ \text{HO} \end{array} \right\}$ (Liebig.)

FUMARIC ACID.

A monobasic acid. Formula, $\text{C}_4\text{HO}_3 + \text{HO}$. Symb. $\overline{\text{Fu}}$. Discovered as a product of the action of heat on malic acid by Lassaigne, and analyzed by Pelouze; in the *Fumaria officinalis* by Winkler, and in Iceland moss by Schoedler. Demarçay first proved the identity of the acid of the fumaria with that derived from malic acid.

It is best obtained by keeping malic acid for a long time heated a few degrees beyond its melting point, when the liquid is gradually converted into a crystalline mass, from which cold water removes any unchanged malic acid. It is also obtained by heating maleic acid in the same way; and some salts of malic acid, when heated, are converted into salts of fumaric acid.

From the juice of *Fumaria officinalis* it is precipitated as fumarate of lead by the addition of acetate of lead. The same salt may be obtained from Iceland moss by digesting it with milk of lime, and adding acetate of lead to the filtered solution. The fumarate of lead is then suspended in water, and decomposed by sulphuretted hydrogen. The impure crystals first obtained are purified by solution in hot nitric acid, which on cooling deposits the fumaric acid pure and colourless.

Fumaric acid forms fine soft micaceous scales, soluble in 200 parts of cold water, more soluble in hot water and in alcohol. When heated a small portion sublimes, but the greater part is decomposed.

Fumaramide.— $\text{C}_4\text{HO}_2 + \text{Ad.}$ (Hagen.) Formed by the action of aqua ammoniæ on fumarate of oxide of ethyle. A snow-white powder, which is slowly dissolved by long boiling in water. By acids and alkalis it is resolved, like other amides, the elements of water being assimilated, into ammonia and the acid.

The salts of fumaric acid are for the most part crystallizable. It forms with ammonia an acid salt in long prisms, $2\overline{\text{Fu}}, \text{AdH}_2\text{O}, \text{HO}$. Its salts with the oxides of lead and silver have exactly the same composition in 100 parts as the corresponding salts of maleic acid. Their formulæ are $\text{C}_4\text{HO}_3, \text{PbO}$, and $\text{C}_4\text{HO}_3, \text{AgO}$.

ACIDS OF UNKNOWN CONSTITUTION.

The acids now to be described are those whose composition is known, but in regard to which it is uncertain whether they are to be considered as monobasic or polybasic.

KINIC ACID.

Syn. Quinic Acid. Chinic Acid.—Formula, $C_7H_4O_4, 2HO?$ or $C_{14}H_{11}O_{11}, HO?$ This very remarkable acid occurs in cinchona bark. It is obtained in the manufacture of sulphate of quinine, in the form of kinate of lime, from which the lime is easily separated by means of oxalic acid. The liquid filtered from the oxalate of lime yields, on evaporation, the kinic acid in crystals. The lime may also be removed by sulphuric acid, and any adhering sulphate of lime separated by alcohol.

The salts of kinic acid are somewhat anomalous. Thus there is a salt of lead, $C_7H_4O_4, 2PbO$, and a salt of copper, $C_7H_4O_4, CuO, HO$, while the crystals of kinic acid are $C_7H_6O_6$. All this would lead to the conclusion that the acid was a bibasic one, $C_7H_4O_4, 2HO$. But the kinate of lime and the kinate of silver, both quite neutral salts, are $C_{14}H_{11}O_{11}, CaO$, and $C_{14}H_{11}O_{11}, AgO$, as if the acid were monobasic, $C_{14}H_{11}O_{11}, HO = C_{14}H_{12}O_{12}$. If we assume the acid to be quadribasic, we can then bring all the above salts into one series.

Thus,—Kinic Acid would be	.	.	$C_{14}H_8O_8, 4 HO.$
Kinate of Lead	.	.	$C_{14}H_8O_8, 4 PbO.$
Kinate of Copper	.	.	$C_{14}H_8O_8 \left\{ \begin{array}{l} 2CuO \\ 2HO. \end{array} \right.$
Kinate of Lime	.	.	$C_{14}H_8O_8 \left\{ \begin{array}{l} CaO \\ 3HO. \end{array} \right. + 10aq.$
Kinate of Silver	.	.	$C_{14}H_8O_8 \left\{ \begin{array}{l} AgO \\ 3HO. \end{array} \right.$

But the objection to this view is, that, if this be the true constitution of the acid, the salts of lime and silver ought to be very acid, instead of being quite neutral.

PRODUCTS OF THE DECOMPOSITION OF KINIC ACID.

When kinic acid or kinate of lime is distilled with diluted sulphuric acid and peroxide of manganese, there is obtained a new compound, called *kinone*, as a sublimate of fine golden yellow crystals, soluble in water, and very volatile, having a pungent smell in the state of vapour. Their composition is $C_{25}H_8O_8$. When acted on by reducing agents,

it takes up 2 and 4 eq. of hydrogen, forming two new compounds, green and white hydrokinone. The *green hydrokinone*, $C_{25}H_{10}O_8$, is one of the most beautiful compounds known to chemists, forming long prisms of the most brilliant gold-green metallic lustre, surpassing those of murexide in beauty. It is best formed by adding a few drops of sulphurous acid to a solution of kinone. When an excess of sulphurous acid is used, the *white hydrokinone*, $C_{25}H_{12}O_8$, is formed, which crystallizes in six-sided prisms. When acted on by oxidizing agents, the solution of white hydrokinone becomes dark-red, nearly black, and almost immediately deposits the splendid crystals of the green compound. The latter is also formed by simply mixing solutions of kinone and white hydrokinone, being intermediate in composition between those bodies. Wöhler, to whom we are indebted for most of our knowledge in regard to these very curious compounds, has described a series of bodies obtained from the above by the action of hydrochloric acid, chlorine, and sulphuretted hydrogen. The following tabular view contains the names and composition of these substances, as far as we yet know them.

Kinone	C_{25}	H_6	O_8
Green Hydrokinone	C_{25}	H_{10}	O_8
White Hydrokinone	C_{25}	H_{12}	O_8
Chlorohydrokinone	C_{25}	$\left\{ \begin{array}{l} H_{10} \\ Cl_2 \end{array} \right.$	O_8
Chlorokinone	C_{25}	$\left\{ \begin{array}{l} Cl_2 \\ H_6 \end{array} \right.$	O_8
Brown Sulphohydrokinone	C_{25}	H_{11}	O_7S_4
Yellow ditto	C_{25}	H_{12}	O_7S_6
Brown Chlorosulphokinone	C_{25}	H_8	$ClO_8S_4?$
Orange ditto	C_{25}	H_6	$ClO_8S_4?$

It will be observed, that in all these formulæ the carbon remains unaltered, and that several are instances of pure substitution, as $C_{25}H_8O_8$ compared with $C_{25}\left\{ \begin{array}{l} H_6 \\ Cl_2 \end{array} \right\}O_8$, and $C_{25}H_{12}O_8$ compared with $C_{25}\left\{ \begin{array}{l} H_{10} \\ Cl_2 \end{array} \right\}O_8$. We can also see the relation of the sulphohydrokinones to kinone, if we express them as follows :— $C_{25}H_8\left\{ \begin{array}{l} O_7 \\ S \end{array} \right\} + 3HS$; and $C_{25}H_8\left\{ \begin{array}{l} O_7 \\ S \end{array} \right\} + 4HS$.

Gerhardt, on theoretical grounds, has suggested that the formula of kinone should be $C_{12}H_4O_4$, that of white hydrokinone $C_{12}H_6O_4$, and that of the green crystals, $C_{12}H_5O_4$, or rather $C_{24}H_{10}O_8$. It will be seen, that, when reduced to the same equivalent, these formulæ differ from those of Wöhler by only 1 eq. of carbon. But the chief argument in favour of the formulæ of Gerhardt is, that they explain more readily the production of these bodies from kinic acid. Thus, kinic

acid, $C_{14}H_{12}O_{12}$, with 4 eq. of oxygen, yields 2 eq. of carbonic acid, 8 of water, and 1 of kinone, $C_{12}H_4O_4$. By the action of sulphurous acid and other deoxidizing agents water is decomposed, and 2 eq. of hydrogen added to kinone yield white hydrokinone, $C_{12}H_6O_4$; while the addition of only 1 eq. of hydrogen yields the green compound, $C_{12}H_5O_4$. Besides the superior simplicity of these formulæ, they enable us to explain the fact, that, when kinic acid is distilled, there are formed carbonic acid, water, white hydrokinone, benzoic acid, and its isomeric hyduret of salicyl, and, finally, carbolic acid or hydrate of phenyl. Thus, 3 eq. of kinic acid, $3(C_{14}H_{12}O_{12})$, amount to $C_{42}H_{36}O_{36}$; and

1 eq. of Benzoic Acid		
or Hyduret of Salicyl	.	= $C_{14}H_6O_4$
1 eq. Carbolic Acid	.	= $C_{12}H_6O_2$
1 eq. White Hydrokinone	.	= $C_{12}H_6O_4$
4 eq. Carbonic Acid	.	= $C_4H_2O_8$
and 18 eq. of Water	.	= $H_{18}O_{18}$
amount to	.	$C_{42}H_{36}O_{36}$

The analysis of kinone by Woskresensky led him to the formula advocated by Gerhardt, $C_{12}H_4O_4$; but future researches must decide whether that or the formula of Wöhler, who alone has examined the other products, be the correct one.

It is interesting to observe the relation between kinic acid and the benzoyl and salicyl series, as shewn in the products of its distillation. Indeed, as benzoyl and salicyl both contain 14 eq. of carbon, and as the destructive distillation commonly gives rise to products of a less complex nature and lower atomic weight, we might almost suppose the true equivalent of kinic acid to contain 28 eq. of carbon. It must be observed, however, that we are not acquainted with any compound bearing the same relation to kinic acid that hyduret of benzoyl does to benzoic acid. Kinone and the hydrokinones belong to the series containing 12 eq. or 24 eq. of carbon; and carbolic acid, another member of this series, also appears among the products of the distillation of kinic acid.

Finally, it is proper to point out, that there seems, according to Lerch's observations, to be some relation between kinic acid and gallic acid (C_7 or C_{14}), meconic acid (C_{14}) and chelidonic acid (C_{14}). A substance, pyrocatechine, which is obtained by the action of heat on catechu, (a body related to tannic and gallic acids,) and which has the properties of white hydrokinone, may possibly be identical with it.

VOLATILE OILY ACIDS.

We now come to a very interesting class of acids, which are very widely distributed throughout both the vegetable and the animal king-

doms. Recent researches have not only added greatly to their number, but have shewn that a large proportion of them form a natural series of what may be called homologous bodies. This class of acids includes most of the volatile oily acids; and we shall in the first place describe those which form the remarkable series exhibited at p. 700, and afterwards such of the volatile oily acids as do not belong to that series.

It will be remembered that the characteristic of the series alluded to is this, that each hydrated acid contains an equal and even number of eq. of carbon and hydrogen, increasing regularly by 2 in the scale; and also that in the hydrated acids the oxygen invariably amounts to 4 eq.; while, as the acids are all monobasic, the oxygen in the anhydrous acids amounts of course to 3 eq. For the convenience of the reader, the series is here repeated.

1. Acetic Acid	$C_4 H_4 O_4 = C_4 H_3 O_3, HO.$
2. Metacetic Acid .	$C_6 H_6 O_4 = C_6 H_5 O_3, HO.$
3. Butyric Acid .	$C_8 H_8 O_4 = C_8 H_7 O_3, HO.$
4. Valerianic Acid .	$C_{10} H_{10} O_4 = C_{10} H_9 O_3, HO.$
5. Caproic Acid .	$C_{12} H_{12} O_4 = C_{12} H_{11} O_3, HO.$
6. Ceanthyllic Acid .	$C_{14} H_{14} O_4 = C_{14} H_{13} O_3, HO.$
7. Caprylic Acid .	$C_{16} H_{16} O_4 = C_{16} H_{15} O_3, HO.$
8. Pelargonic Acid .	$C_{18} H_{18} O_4 = C_{18} H_{17} O_3, HO.$
9. Capric Acid .	$C_{20} H_{20} O_4 = C_{20} H_{19} O_3, HO.$
10. * * *	* * *
11. Lauric Acid .	$C_{24} H_{24} O_4 = C_{24} H_{23} O_3, HO.$
12. Cocinic Acid .	$C_{26} H_{26} O_4 = C_{26} H_{25} O_3, HO.$
13. Myristic Acid .	$C_{28} H_{28} O_4 = C_{28} H_{27} O_3, HO.$
14. * * *	* * *
15. Palmitic and } Ethalic Acids }	$C_{32} H_{32} O_4 = C_{32} H_{31} O_3, HO.$
16. Margaric Acid .	$C_{34} H_{34} O_4 = C_{34} H_{33} O_3, HO.$

There are, it will be seen, two blanks in the series, but little doubt can be entertained that these will soon be filled up. The first acid is volatile, but not oily, and has, with the second, been already described; but that they belong to the series is evident from this, that the second acid partakes of the properties of the first quite as much as of those of the third, and, although decidedly oily, yet forms a perfect connecting link between the acid below it and those above it.

The oily acids of this series, beginning with butyric acid, have many properties in common. They are all volatile, and their boiling points, as far as known, rise regularly in proportion as the amount of C_2H_2 increases. They are seldom found separately: in butter six of them have been observed; two or three have been found in cocoa-nut oil; and nine of them have been detected by Redtenbacher among the products of the oxidation of oleic acid by nitric acid. In butter they occur combined with glycerine, forming neutral oils, such as butyrine. The properties of those placed near each other in the scale are so si-

milar, that their separation is a matter of great difficulty, and is only accomplished by means of the more or less sparing solubility of their barytic salts, which property, like the boiling point of the acids, varies with the composition. They all combine with oxide of ethyle with extreme facility, yielding in general fragrant ethers, some of which are most probably the cause of the fragrance of high-flavoured fruits. Further, several of them, more particularly acetic, metacetic, butyric and valerianic acids, are formed from starch, or rather from grape sugar, when made to undergo peculiar forms of fermentation or putrefaction, as well as from animal matter under somewhat similar circumstances. There can be no doubt that all of them are formed in vegetables by the deoxidation of sugar, or of carbonic acid and water. All these circumstances plainly indicate a natural connexion between these remarkable acids.

Our space will only permit us to describe the individual acids very briefly, for which reason we have prefixed the general characters of the class.

VOLATILE ACIDS OF BUTTER.

In the butter of the cow and the goat four volatile acids occur in small quantity, besides the fatty matter which constitutes the chief part of the butter. These acids, three of which were discovered by Chevreul, are named Butyric, Caproic, Caprylic, and Capric acids.

When butter is saponified by boiling with caustic alkalies, and the resulting soap is decomposed by an excess of tartaric acid, certain fatty acids, insoluble in water, are separated. The water retains in solution the tartrate of the alkali, oxide of glycercyle, and the volatile acids now under consideration. The solution when distilled yields a product containing the four acids. It is neutralized by hydrate of baryta, and evaporated to dryness.

The dry mass is boiled with 5 or 6 parts of water, which dissolve a part, consisting of caproate and butyrate of baryta, while the undissolved portion contains caprylate and caprate of baryta. The two salts in each portion are separated by crystallization. The butyrate is the most soluble, the caproate less so; the caprylate is sparingly soluble, and the caprate almost insoluble, in cold water. (Chevreul, Lerch.)

BUTYRIC ACID.

Formula of the Anhydrous Acid . . .	$C_4H_7O_2$?
„ „ Hydrated Acid . . .	$C_4H_7O_2 + HO$?

This acid is obtained from the butyrate of baryta, prepared as above from butter, by the cautious addition of sulphuric acid. But it is now

much more economically prepared from butyrate of lime, a salt which may be procured in any quantity by causing sugar to undergo a peculiar fermentation, which may be called the butyric fermentation.

A moderately strong solution of sugar is mixed with a little pure cheese or pressed curd and a considerable quantity of prepared chalk, and the whole is placed in a temperature of from 85° to 105° . The cascade enters into a state of decomposition, and it commonly happens that the sugar first undergoes the change by which it is converted into lactic acid. This part of the process is not necessarily accompanied by the evolution of any gas derived from the sugar, nor, according to Pelouze and Gelis, by the formation of mannite and mucilage, as in the viscous fermentation. We may therefore admit a lactic fermentation in which 1 eq. of grape sugar $C_{12}H_{14}O_{14}$, or of milk sugar $C_{12}H_{12}O_{12}$, or of cane sugar $C_{12}H_{11}O_{11}$, the first losing 2 eq. and the last gaining 1 eq. of water, is split up into 2 eq. of lactic acid, $2(C_6H_6O_6)$. The lactic acid as it is formed unites with the lime of the chalk, forming lactate of lime, while carbonic acid is disengaged. The liquid often becomes nearly solid from the separation of the lactate of lime, which is but sparingly soluble. But if the mass be left in the same temperature, a further change takes place. The lactate of lime gradually dissolves again, carbonic acid and hydrogen are given off, and this time the carbonic acid is not derived from decomposed chalk, as it is the lactate of lime already formed which is decomposed. When the change is complete, which takes place in a very variable time, the liquid, filtered from the remaining cheese and the excess of chalk, is found to contain nothing but butyrate of lime. In some cases the butyric fermentation sets in so rapidly, that the lactate of lime seems to be decomposed as fast as it is formed; but most frequently the changes are successive. It is easy to see how the butyric acid may be derived from the lactic acid, for 2 eq. of lactic acid $C_{12}H_{12}O_{12}$, are equal to 1 eq. of butyric acid $C_8H_7O_3, HO$, 4 eq. of carbonic acid $4CO_2$, and 4 eq. of hydrogen.

This mode of formation of butyric acid has been described somewhat fully, because of its great importance in reference to the theory of the formation of the oily and fatty acids in the animal body, as well as in vegetables. Butyric acid is a true oily acid, found in butter in combination with glycerine; and it is clear, that the theory of its formation from sugar or starch, when fully known, will include that of all other oily acids, more especially of those belonging to the series now under consideration. In the production of butyric acid, 1 eq. of sugar, $C_{12}H_{12}O_{12}$, loses 4 eq. of carbon, 4 of hydrogen, and 8 of oxygen. The process, therefore, is one of deoxidation, which is carried farther

in all the following acids than in butyric acid, for in these acids the proportion of oxygen to carbon and hydrogen regularly diminishes as we ascend the scale.

The butyrate of lime, obtained by the above process, is distilled with a slight excess of diluted hydrochloric acid. The distilled liquid, which is a solution of butyric acid in water, is mixed with chloride of calcium. As this salt dissolves, the butyric acid rises to the surface as an oil, which, after having been left for some time in contact with fragments of chloride of calcium, is rectified. As soon as the temperature of the boiling acid rises to 327° , the receiver is changed, and what passes at that temperature is pure hydrated butyric acid.

It is a colourless, mobile, oily fluid, of sp. gr. 0.963 at 60° , boiling at 327° , which has a burning acid taste, and a strong peculiar smell, analogous, when much diluted, to that of rancid butter.

With bases, butyric acid forms salts, many of which crystallize with facility. They have often, especially when moist, a slight smell of the acid. As the acid is monobasic there is but one series of salts, the general formula of which is $\overline{\text{Bu}}, \text{MO}$.

The *butyrates of potash and ammonia* are deliquescent. *Butyrate of lime* is very soluble in cold water, but, when the solution is warmed, the salt separates in small crystals, being less soluble in hot water. Butyrate of baryta forms large transparent crystals, which, when thrown on water, exhibit the rotatory movements of camphor.

Butyrate of oxide of ethyle or butyric ether is instantly formed when 2 parts of butyric acid, 2 of alcohol, and 1 of sulphuric acid are mixed. Heat is produced, and the ether rises to the surface. It is washed with water, dried by chloride of calcium, and rectified. It has a pleasant ethereal odour, and is used to give to grain spirits the flavour of rum, a small quantity of it having, it is said, this effect.

Butyric acid combines as readily with oxide of methyle and with glycerine as with ether. The butyrate of glycerine appears to be the same oily compound, butyrine, which exists ready formed in butter in small proportion, and, if so, is the first instance of a neutral oil formed artificially, such as occurs in the animal and vegetable fats.

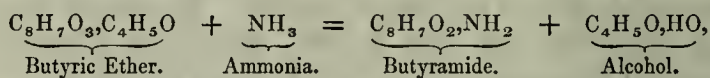
Butyrone.—When butyrate of lime is heated there are formed carbonate of lime and an oily liquid, butyrone, $\text{C}_7\text{H}_7\text{O}$. It is analogous to acetone, and is butyric acid, $\text{C}_8\text{H}_7\text{O}_3$, minus 1 eq. of carbonic acid CO_2 .

Butyrone yields, with nitric acid and chlorine, new compounds, in which hydrogen is replaced by nitrous acid and chlorine. The compound formed by nitric acid is an acid, nitrobutyric acid. (Chancel.)

Butyral.—This name is given by Chancel to a liquid found among

the products of the distillation of butyrate of lime. It is more volatile than butyrene. Its formula is $C_8H_8O_2$, and it therefore bears the same relation to butyric acid that aldehyde does to acetic acid. It is actually oxidized, and converted into butyric acid when heated with fuming sulphuric acid, which is reduced to sulphurous acid. $C_8H_8O_2 + 2SO_3 = C_8H_7O_3,HO + 2SO_2$.

Butyramide.—This compound is slowly formed when butyric ether is acted on by ammonia.



Butyric acid occurs among the products of putrefying fibrine and caseine. It is also found in the fluid of *Sauerkraut* and in the fermented juice of cucumbers, along with lactic acid. It would appear to be of very frequent occurrence, and it probably plays an important part in the metamorphoses of organic compounds while contained in living organisms, whether animal or vegetable. It has been already mentioned that butyric acid is one of the products of the action of nitric acid on oleic acid.

CAPROIC ACID.

This acid is extracted from the caproate of baryta, which forms, along with the butyrate, the more soluble portion of the saline mass obtained from the volatile oily acids of butter. Caproic acid is analogous to butyric acid, but its boiling point is considerably higher, at 396° . Its odour recalls that of sweat. Its formula is $C_{12}H_{11}O_3,HO$, and it is monobasic. Its salts are little known, as it occurs in a very small proportion in butter. The caproate of baryta crystallizes in long slender prisms, grouped together in spherical masses. Caproate of oxide of ethyle is fragrant, and is as easily formed as the corresponding butyrate.

CAPRYLIC ACID.

This acid is extracted from the caprylate of baryta, which along with the caprate forms the less soluble portion of the saline mass above mentioned. Caprylic acid is analogous to the two preceding acids, being oily, volatile, boiling, however, at a still higher temperature, at 465° , and solidifying below 40° . Its salts are little known, as it forms only a small proportion of the volatile acids of butter, and has only recently been recognized as a distinct acid by Lerchl. It is monobasic, and its formula is $C_{16}H_{15}O_3,HO$. The caprylic ether has a fragrant smell, like that of pine-apples.

CAPRIC ACID.

This acid is separated in the usual way from the caprate of baryta, which forms the least soluble part of the saline mass from which the three preceding acids, as well as this one, are obtained. It becomes solid at 44° , and the crystals, once formed, remain solid even at 60° . Above that temperature it is a liquid boiling about 534° , and has a strong rank smell, resembling that of the goat. Its salts are crystallizable, and that of baryta is nearly insoluble in cold water. A solution of this salt, if kept, becomes turbid and acquires the smell of *fromage de Roquefort*. This acid, as well as the three preceding ones, has been recently found by Redtenbacher among the products of the action of nitric on oleic acid. Its formula is $C_{20}H_{19}O_3, HO$.

VACCINIC ACID.

In examining the volatile acids of butter in 1842, Lerch observed that the more soluble portion of the saline mass obtained by neutralizing with baryta the distilled acids, instead of yielding, as usual, first caproate, and then butyrate of baryta by crystallization, gave crystals of a new salt, which he found to contain a new acid, called by him *vaccinic acid*. This acid, however, was not obtained in a separate state, for when the salt was decomposed by sulphuric acid, and the oily acid distilled, and again neutralized with baryta, it yielded caproate and butyrate in atomic proportions. The vaccinate of baryta could be crystallized without change; but if exposed to the air for a long time, till it loses the strong smell of butter which it possesses at first, it yields, when re-dissolved and evaporated, only caproate and butyrate. It is evident, therefore, that its composition must be intermediate between that of caproic and that of butyric acid. The analysis of Lerch led him to the formula $C_{20}H_{18}O_5, 2BaO$, for the salt of baryta; and if to this we add 1 eq. of oxygen from the air, we have $C_{20}H_{18}O_6, 2BaO = C_8H_7O_3, BaO + C_{12}H_{11}O_3, BaO$, that is, 1 eq. butyrate, and 1 eq. caproate of baryta. As oxide of silver produces the same change as exposure to air, this explanation of the conversion of vaccinic into caproic and butyric acids is probably correct. The causes which lead to the formation of this acid instead of the others are quite unknown. The summer of 1842, when the vaccinic acid replaced the caproic and butyric acids in the butter examined by Lerch, was, in Bohemia, where his researches were made, unusually dry. In 1843, he could not obtain a trace of vaccinate of baryta, but only caproate and butyrate in its place.

The four acids usually found in butter are evidently related to each other; in the following table this relation is seen :—

Hydrated Butyric Acid	$C_8H_8O_4 = 8CH + O_4.$
„ Caproic Acid	$C_{12}H_{12}O_4 = 12CH + O_4.$
„ Caprylic Acid	$C_{16}H_{16}O_4 = 16CH + O_4.$
„ Capric Acid	$C_{20}H_{20}O_4 = 20CH + O_4.$

It will be observed that they differ only in the amount of CH which they contain; and their boiling points and densities vary in a similar ratio. Thus, the boiling point of caproic acid is higher than that of butyric acid; and the boiling points of caprylic and capric acids rise by an equal amount above that of the acid next below each respectively, so that the difference between the boiling point of capric acid and that of butyric acid is three times that between the boiling points of caproic and butyric acids. According to Kopp and Fehling, if we express the general formula of these acids by $(CH)_n + O_4$, then, for every rise of twice unity in n , the boiling point rises about 34.5° . It may also be remarked, that n in these four acids is divisible by 4; but we shall see that acids exist which occupy the intermediate points, and in which n is divisible not by 4, but by 2. This relation only holds between bodies of similar constitution, as hydrated acids, for example, or the ethers of those acids, each considered separately. But where bodies of different constitution are compared, as when the hydrated acids are compared with the ethers, it no longer holds. Thus, butyric acid and acetic ether, which are isomeric, have different boiling points; and the same is true of caproic ether and butyric acid, of caprylic ether and caproic acid, of capric ether and caprylic acid, all of which are respectively isomeric. The density of vapour and the atomic volume of these and similar compounds, as well as their boiling points, are only connected by uniform laws in the case of bodies of like constitution; so that, while we can predict these properties in any of the hydrated acids of this class, if we know them in one acid, or in any ether of these acids, if we know them in one such ether, we cannot deduce the properties of the acid from those of an ether, or *vice versa*.

VALERIANIC ACID.

Formula of the Anhydrous Acid $C_{10}H_{10}O_3.$
 „ of the Hydrated Acid $C_{10}H_{10}O_3.HO.$

Symb. $\overline{Va.}$ Formula of its Salts $\overline{Va.}MO.$

This acid has already been mentioned as formed by the action of caustic potash on hydrated oxide of amyle, or oil of potato spirit, and as existing ready formed in the root of *Valeriana officinalis*. There

can be little doubt that the oil of potato spirit is derived from starch or sugar, a part of which undergoes this change, while the rest is resolved into alcohol and carbonic acid. As the oil bears to valerianic acid exactly the same relation that alcohol does to acetic acid, we may consider valerianic acid as a product of oxidation of the oil; and as thus indirectly formed, like butyric acid, by a peculiar fermentation of sugar. Valerianic acid has also been observed among the products of the putrefaction of caseine, and among the products of the oxidation of gelatine by chromic acid. Liebig has also shewn, that, when caseine is oxidized by fusion with hydrate of potash, valerianic acid is one of the products; and, lastly, Redtenbacher has found it among the acids formed by the action of nitric acid on oleic acid. It has also been shewn to be the acid found by Chevreul in train oil, and in the berries of *Viburnum opulus*, and called by him Phocenic acid.

Valerianic acid would, therefore, appear to be widely distributed, and to be a frequent result of the metamorphoses of organic compounds. It is here mentioned as occupying the position exactly between butyric and caproic acids in the series of volatile oily acids, of the formula $(\text{CH})_n + \text{O}_4$.

Besides the hydrated acid formerly mentioned, there exists another hydrate, $\overline{\text{Va}}, 3\text{HO}$, which is obtained when a strong solution of any of its salts is decomposed by an acid.

The salts of valerianic acid are generally soluble, and have a slight smell of valerian. The valerate of oxide of ethyle, $\overline{\text{Va}}, \text{AeO}$, may be obtained by the action of heat on a mixture of alcohol, oil of vitriol, and valerianic acid. It is an oily liquid, with a penetrating smell of fruit and of valerian; of sp. gr. 0.894. (Otto.)

The valerate of oxide of amyle, or at least a liquid having the composition $\text{C}_{20}\text{H}_{40}\text{O}_4 = \overline{\text{Va}}, \text{AylO}$, is obtained by the action of heat on a mixture of oil of vitriol, hydrated valerianic acid, and bichromate of potash. (Dumas and Stass.) It is an oily liquid, which requires a careful investigation. The valerates of metallic oxides are anhydrous, and their general formula is $\overline{\text{Va}}, \text{MO}$.

ACTION OF CHLORINE ON VALERIANIC ACID.

Chlorovalerisic Acid.—When valerianic acid is acted on in the dark by chlorine gas, a new acid is produced, the formula of which is $\text{C}_{10}\text{H}_7\text{Cl}_3\text{O}_4$. If we compare this with hydrated valerianic acid, $\text{C}_{10}\text{H}_{10}\text{O}_4$, it appears that chlorovalerisic acid may be regarded as valerianic acid in which 3 eq. of hydrogen are replaced by 3 eq. of chlorine,

without the general character of the compound being changed. The new acid is a viscid liquid, devoid of smell, and is easily soluble in alkalis.

Chlorovalerosic Acid.—When the action of chlorine is assisted by sunlight, another new acid is formed, the formula of which is $C_{10}H_5Cl_4O_3$ in the anhydrous state. It is anhydrous valerianic acid, $C_{10}H_9O_3$, in which 4 eq. of hydrogen have been replaced by 4 eq. of chlorine. Its hydrate is $C_{10}H_5Cl_4O_3 + 3HO$. With bases it forms salts very similar to the salts of valerianic acid. The chlorovalerosate of silver is $C_{10}H_5Cl_4O_3, AgO$.

These very remarkable compounds were discovered by Dumas and Stass. They are good examples of the law of substitution proposed by Dumas, the original type of the compound being retained.

According to Löwig, valerate of lime, when distilled, yields an oily liquid, valerone, $C_9H_9O = C_{10}H_9O_3 - CO_2$. The same chemist states that valerianic acid is in the valerian combined with oxide of glyceryle, producing a peculiar fat; but this is doubtful.

CENANTHYLIC ACID.

Formula of the Anhydrous Acid, $C_{14}H_{13}O$.
 „ Hydrated Acid, $C_{14}H_{13}O, HO$.

This acid was first discovered by Tilley among the products of the action of nitric acid on castor oil. It has been recently found by Redtenbacher among the volatile acids formed by the action of nitric acid on oleic acid. It has not yet been observed as a natural product. It stands between caproic and caprylic acids, and is very analogous to those acids. Cēnanthylie ether has a fragrant aromatic smell.

Cēnanthole.—Bussy observed, that, when castor oil is distilled, there is formed in considerable quantity a liquid compound which he calls Cēnanthole. It boils at 312° ; and its formula is $C_{14}H_{14}O_2$. It thus bears the same relation to cēnanthylie acid that aldehyde does to acetic acid.

Aldehyde, C^4H_3O, HO Acetic Acid, $C^4H_3O_3, HO$.
 Cēnanthole, $C_{14}H_{13}O, HO$. Cēnanthylie Acid, $C_{14}H_{13}O_3, HO$.

This compound may also be viewed as a compound of cēnanthylie acid, with an oxide analogous to oxide of ethyle, a compound, therefore, corresponding to acetic ether.

Acetyle of Oxide of Ethyle $C_4H_5O + C_4H_3O_3$.
 Cēnanthole $2(C_{14}H_{14}O_2) = C_{14}H_{15}O + C_{14}H_{13}O_3$.

The oxide, $C_{14}H_{15}O$, has not been obtained; but the experiments of Williamson render it probable that when cēnanthole is acted on by

potash, the hydrate of that oxide, a body corresponding to alcohol, is produced, while the potash is found to be combined with ænanthyllic acid.

This latter view of the constitution of ænanthole makes it quite analogous to cetine, which is the cetylate of oxide of cetylene. But it is evident that cetine may also be viewed as a compound having the same relation to cetylic acid, that aldehyde has to acetic acid. Aldehyde is polymeric with acetic ether; but in the cases of ænanthole and cetine we cannot positively ascertain, as only one compound is known, whether that compound be analogous in constitution to aldehyde or to acetic ether.

PELARGONIC ACID.

This acid, which stands between caprylic and capric acids, has been found in the juice of *Pelargonium roseum*, and occurs also among the products of the oxidation of oleic acid by nitric acid. It is as yet but little known; but its formula appears to be $C_{18}H_{17}O_3.HO$. Its properties seem to be exactly intermediate between those of caprylic and capric acids. It is semi-solid at ordinary temperatures.

In the preceding pages we have briefly described the volatile oily acids of the series $(CH)_n + O_4$ from butyric acid, in which $n = 8$, to capric acid, in which $n = 20$. The acids higher in the scale, being rather fatty than oily, will be more conveniently described farther on, after we have noticed some other volatile oily acids, not belonging to that series. In the meantime, it may be remarked that the acids here described afford in their origin and in their properties a most instructive example of the close relation between the properties of different compounds of like constitution and their composition. It is a curious fact that the four acids which occur in butter have $n = 8, 12, 16$, and 20 respectively; that is, in all of them, n is divisible by 4 ; while the salts of these four acids with baryta, although of different solubility, all crystallize in slender prisms; while the corresponding barytic salts of the three acids in which $n = 10, 14$, and 18 respectively, in which therefore n is divisible not by 4 but by 2 , all crystallize in broad plates or scales. This character is of great use in separating these acids. (Redtenbacher.)

Hircic Acid, observed by Chevreul in the fat of the goat, appears to be a mixture, probably of capric and caprylic acids. *Phocenic*, or *Delphinic Acid*, found by the same chemist in the fat or oil of the whale, and in the berries of *Viburnum opulus*, has been ascertained to be valerianic acid.

SABADILLIC ACID.

Syn. Cevadic Acid.—Discovered by Pelletier and Caventon in the seeds of *Veratrum Sabadilla*. From the oil which ether extracts from the seeds, the sabadillate of baryta is obtained in the same way as butyrate of baryta from butter. When this salt is heated with concentrated phosphoric acid, the sabadillic acid sublimes in white needles, which are fusible at 70° , and have the smell of butyric acid. Its composition is unknown.

CROTONIC ACID.

Syn. Iatrophic Acid.—Discovered by Pelletier and Caventon in the seeds of *Croton tiglium*. It is obtained from the oil (croton oil) exactly in the same way as the preceding acid. It is solid, very volatile, has a pungent and nauseous smell, a burning taste, and is very poisonous. Croton oil contains some free crotonic acid. The salts of crotonic acid are generally soluble and crystallizable, and have no smell. The composition of the acid is unknown.

CAMPHORIC ACID.

Formula of the anhydrous acid, $C_{10}H_7O_3$. Symb. $\overline{Ca}$. (Malaguti, Laurent, Walter.)

Formula of the hydrated acid, $C_{10}H_7O_3 + HO$. Symb. $\overline{Ca}, HO$. Discovered by Kosegarten. The anhydrous acid was first obtained by Malaguti and Laurent.

To prepare it, camphor is digested with a large excess of nitric acid till it is entirely dissolved, fresh acid being added as often as may be required. The acid solution, being evaporated, yields impure camphoric acid. It is purified by combining it with potash, which separates any camphor that may have escaped oxidation. The camphorate of potash is then decomposed by nitric acid, when pure hydrated camphoric acid crystallizes. It forms small scales or needles, of a taste at first sour, then bitter. When distilled, it is resolved into water and anhydrous acid.

The salts of camphoric acid, with the alkalis and alkaline earths, are soluble and crystallizable. The other camphorates are insoluble, or sparingly soluble.

Camphorate of Ammonia. *a.* Neutral. $\overline{Ca}, AdH_2O$. *b.* Acid.
 $3\overline{Ca} + \left\{ \begin{array}{c} 2AdH_2O \\ HO \end{array} \right\} + 9aq.$

Camphorate of Oxide of Ethyle. a. Acid. $2\overline{\text{Ca}}\left\{\begin{smallmatrix}\text{AeO} \\ \text{HO}\end{smallmatrix}\right\}$. (Malaguti.) Obtained by heating camphoric acid, alcohol, and sulphuric acid together. The addition of water causes the new compound to separate. It is a colourless syrupy liquid, which, by boiling with water, is resolved into camphoric acid and neutral camphorate of oxide of ethyle. It forms with alkalies and bases in general a series of double salts, in which the atom of water is replaced by its equivalent of base.

b. Neutral. The neutral camphorate of oxide of ethyle, or camphoric ether, $\overline{\text{Ca}},\text{AeO}$, is obtained by dissolving in alcohol the product of the distillation of the acid salt. When the alcohol deposits no more crystals of camphoric acid, the addition of water separates the camphoric ether as an oily liquid, sp. gr. 1.029. It boils at 545° . Its formula is $\overline{\text{Ca}},\text{AeO}$. When acted on by chlorine, it yields chlorocamphoric ether, $\overline{\text{Ca}},\text{C}_4\text{H}_3\text{Cl}_2\text{O}$. (Malaguti.)

The so-called anhydrous camphoric acid, $\text{C}_{10}\text{H}_7\text{O}_3$, is obtained by crystallizing in alcohol the product of the distillation of hydrated camphoric acid, or of the acid camphorate of ethyle. It forms long, flat, colourless prisms, which have no sour taste. By very long-continued boiling with water it is dissolved, and passes into hydrated acid. (Laurent.)

The existence of anhydrous organic acids is very doubtful. The substances which are supposed to be so are in general but imperfectly known. From the action of heat on tartar-emetic, and from the composition of the succinate of lead lately described by Fehling, it appears that the so-called anhydrous tartaric and succinic acids still contain some water capable of being replaced by bases; and, according to Malaguti, the anhydrous camphoric acid forms different salts from the hydrated acid. It is probable that all such acids differ from the common hydrates, in a manner analogous to that in which the modifications of phosphoric acid differ from each other.

Of the salts of anhydrous camphoric acid but little is known; but they are decidedly distinct from the salts of the hydrated acid, and they do not yield the hydrated acid when decomposed by acids, but a gummy mass, which soon hardens, and is soluble in alcohol.

Anhydrous camphoric acid combines with fuming sulphuric acid, with disengagement of sulphurous acid. When the solution is heated, a large quantity of pure carbonic oxide is disengaged, and an acid is left, which, according to Walter, is $\text{C}_9\text{H}_7\text{O}_5\text{S} = (\text{C}_{10}\text{H}_7\text{O}_3 + \text{SO}_3) - \text{CO}$. This explanation does not account for the production of sul-

phurous acid in the first stage of the process. Walter has analyzed the salts of this new acid, but the results are not quite decisive. Probably a purer and more permanent compound might be obtained by the action of the vapour of anhydrous sulphuric acid on anhydrous camphoric acid. With ammonia anhydrous camphoric acid appears to form two compounds, one of which is probably camphamic acid, and the other camphamate of ammonia, analogous to oxamic acid and oxamate of ammonia.

APPENDIX TO CAMPHORIC ACID.

CAMPHOR AND OIL OF CAMPHOR.

In the camphor-tree of Sumatra and Borneo, (*Dryobalanops camphora*,) and of Japan, (*Persea camphora*,) camphor and oil of camphor are found, chiefly in those parts of the wood which in resinous trees contain the resin. The wood is split up, and the solid masses of camphor are taken out. By distilling the wood with water, an additional quantity of camphor is obtained, along with the volatile oil.

Oil of Camphor.—Formula, $C_{20}H_{16}$. The oil of commerce contains camphor dissolved, which it deposits in crystals by evaporation. By repeated rectification the oil may be obtained colourless: it is a very mobile liquid, refracting light strongly; of sp. gr. 0.91. Its boiling point lies above 212° . It absorbs oxygen from the air. By distillation with nitric acid it yields camphor, which differs from it in containing exactly twice as much oxygen. With hydrochloric acid it forms a neutral solid compound, insoluble in water. Oil of camphor dissolves phosphorus, iodine, and sulphur; and is miscible with sulphuric and acetic acids, fixed and volatile oils, ether and alcohol. It forms a stiff jelly with powdered copal.

Camphor of Laurus camphora.—Formula, $C_{10}H_8O$. (Dumas; Blanchet and Sell.) Obtained as above described. According to Dumas, the crystalline substance deposited by oil of lavender is identical with common camphor. Camphor is also formed by the action of nitric acid on the carbohydrogens of the oils of valerian and sage, on amber, and, finally, on Borneo camphor. Indeed, Gerhardt is of opinion that all these oils yield camphor only in so far as they contain Borneo camphor ready formed. Camphor is a white, crystalline, translucent solid, somewhat tough, but easily pulverized when moistened with alcohol. Its sp. gr. is 0.9857 to 0.996. It melts at 347° , and sublimes entirely with ebullition at 400° . The density of its vapour is 5.317. (Dumas.) It evaporates readily in the air. Fragments of camphor,

when thrown on water, evaporate more rapidly than when dry, and are thrown into a rotatory motion, arising from the simultaneous formation of the vapours of water and camphor.

Camphor is combustible, and burns with a smoky flame. It is soluble in 1000 parts of water, but is said to dissolve easily when boiled with water under increased pressure. Ten parts of alcohol dissolve twelve of camphor. It is also soluble in proof spirit and in ether. The solution in proof spirit (camphorated spirit) is precipitated by water. Fixed and volatile oils, and bisulphuret of carbon, dissolve it. It is miscible by fusion with sulphur and phosphorus. With iodine it forms a brown compound. In chlorine gas it liquefies without apparent decomposition. Oil of vitriol dissolves it; and when the solution is heated, it yields sulphurous acid gas, and an oil smelling of peppermint and camphor. Nitric acid dissolves camphor; and when the solution is boiled, it is gradually converted into camphoric acid.

Camphor is used in medicine, both internally in the form of emulsion, and externally in the form of ointment. Internally it acts as a diffusible stimulant, but in large doses it is poisonous. It increases the solubility of copal in alcohol, and hence is an ingredient in copal varnish.

Camphrone.—When the vapour of camphor is passed over quicklime at a low red heat, a volatile liquid is obtained among the products, which appears to have the formula $C_{30}H_{21}O$. (Fremy.) This is camphrone. If the same experiment be performed at a white heat, the products are naphthaline, $C_{20}H_8$, olefiant gas, marsh gas, and carbonic oxide gas. (Fremy.)

Camphor of Dryobalanops camphora. *Borneo Camphor*.—This variety of camphor is much prized as a remedy for rheumatic affections in Japan and China, and seldom reaches Europe. It occurs in small irregular fragments, heavier than water. Its smell resembles that of common camphor, but is at the same time slightly alliaceous, as is observed when it is wrapped in paper, through which the alliaceous odour passes readily. (Gregory.)

It has been analyzed by Pelouze, who found its formula to be $C_{10}H_9O$, or $C_{20}H_{18}O_2$. This accounts easily for the fact, that it is at once transferred into ordinary camphor when heated with nitric acid. $C_{10}H_9O + NO_5 = C_{10}H_8O + HO + NO_4$.

Borneo camphor is accompanied by an oil, *borneène*, which is isomeric, if not identical, with the oil of camphor, and with the carbohydrogens of most volatile oils. Its formula is $C_{10}H_8$, and the addition of 1 eq. of water converts it into Borneo camphor. This change occurs in the native oil of *Dryobalanops*, and probably also in oil of

camphor, and in the oils of valerian and sage, all of which yield, by oxidation, ordinary camphor.

In most of its external properties Borneo camphor, or *Borneole*, as Gerhardt names it, is similar to the ordinary species of camphor.

ÆNANTHIC ACID.

Formula of the anhydrous acid, $C_{14}H_{13}O_2$. Formula of the hydrated acid, $C_{14}H_{13}O_2.HO$. (Pelouze and Liebig.)

This acid occurs in most fermented liquors, especially in wine and corn spirit, combined with oxide of ethyle. When wine is distilled, this compound passes over at the end of the process in small quantity. By digestion with potash, ænanthate of potash is obtained, and from this salt the acid is separated by sulphuric acid, in the form of an oily liquid, which rises to the surface. At 54° it is semi-solid. It has neither taste nor smell; is insoluble in water, soluble in alcohol and ether. In this state it is the hydrated acid. When distilled, it is resolved into water and anhydrous acid.

Of the salts of ænanthic acid only the ænanthate of oxide of ethyle is well known. This is the oil obtained by distilling wine or other fermented liquors, at the end of the distillation. It is purified from a little free ænanthic acid by heating it with a weak solution of carbonate of potash, when the pure oil rises to the surface. Its formula is $C_{18}H_{18}O_3 = C_{14}H_{13}O_2 + C_4H_5O$. (Pelouze and Liebig; Mulder.) It is a mobile, oily colourless liquid, having a strong smell of wine. Sp. gr. 0.862. It boils at 435° . By the action of potash it is resolved into ænanthic acid and alcohol.

It is to be observed, that this singular compound is not the cause of that peculiar fragrance in certain wines which is called the bouquet or aroma; but, on the contrary, of that somewhat unpleasant smell which is found in every kind of wine, and which is so characteristic, that we can always tell by it whether a bottle or cask has been used for containing wine, even when the vessel has been for some time empty.

ROCCELLIC ACID.

Formula of the crystallized acid, $C_{17}H_{16}O_4$. (Liebig.) Discovered in *Rocella tinctoria* by Heeren. It is extracted from the lichen by ammonia, and the solution precipitated by chloride of calcium. The roccellate of lime is decomposed by weak hydrochloric acid, when the roccellic acid separates. It is purified by solution in ether and crystallization. It forms fine white needles, fusible about 295° . In its

general character it resembles the oily acids. Its salts have been little studied.

VERATRIC ACID.

Formula of the acid in the salt of silver, $C_{18}H_9O_7$. Formula of the hydrated acid, $C_{18}H_9O_7 \cdot HO$. (Schrötter.) Discovered by Merck in the seeds of *Veratrum Sabadilla*. The seeds are exhausted by a mixture of alcohol and sulphuric acid, and the solution precipitated by milk of lime. The veratrate of lime remains in solution. It is decomposed by hydrochloric acid, and the new acid crystallizes. It forms short white transparent prisms, which are soluble in water and alcohol, insoluble in ether. When heated they melt, and are volatilized without residue.

Its salts are for the most part soluble. It forms with oxide of ethyle a crystalline compound, $C_{22}H_{14}O_8 = C_{18}H_9O_7 + C_4H_5O$. (Will.)

CUMINIC ACID.

Formula of the hydrated acid, $C_{20}H_{11}O_3 + HO$. (Gerhardt and Cahours.) To obtain it, Roman oil of cumin is dropped into melted potash, when hydrogen is disengaged, and cuminate of potash is formed. The addition of an acid causes the cuminic acid to separate. The hydrated acid is a white crystallized solid, which is soluble in alcohol and volatile. Its salts are not known.

When heated with baryta, cuminic acid is resolved into 2 eq. carbonic acid, and 1 eq. of an oil analogous to benzole, *cumène*, the formula of which is $C_{18}H_{12}$. It forms new compounds with sulphuric acid and with nitric acid, probably analogous to hyposulphobenzidic acid and to nitrobenzole.

According to Gerhardt and Cahours, Roman oil of cumin is a mixture of two oils, one of which is a carbohydrogen, and the other analogous to the hyduret of benzoyle, having the formula $C_{20}H_{11}O_2 + H$. The radical of this oil they call Cumyle $= C_{20}H_{11}O_2$.

According to Volkel, the common oil of cumin or caraway, from *Carum carui*, contains two oils, analogous to the foregoing; but his analyses do not agree with the above formula. By the action of the air, or by that of sulphuric acid and bichromate of potash, Roman oil of cumin is converted into cuminic acid.

CARYOPHYLLIC ACID.

Syn. Eugenig Acid.—Discovered by Bonastre in oil of cloves, and first obtained in a state of purity by Ettling. Oil of cloves contains this acid, mixed with an oil, $C_{10}H_8$. The addition of potash separates this oil, while caryophyllate of potash is formed. This salt is distilled with sulphuric acid and water, yields the hydrated acid, which is an oily liquid of sp. gr. 1.079, with a strong smell of cloves.

The analyses of this acid, by Böckmann and Ettling, lead to the empirical formula $C_{24}H_{15}O_5$. But a comparison of the salt of baryta with the hydrated acid rather leads to the formula $C_{20}H_{12}O_4 = C_{20}H_{11}O_3 + HO$ for the hydrated acid.

According to Dumas, if the cloves be first treated with alcohol, which dissolves a crystalline substance, caryophylline, and afterwards distilled with water, an acid is obtained, which has the formula $C_{20}H_{13}O_5$, and thus appears to contain 1 at. water more than the acid above mentioned. This latter acid forms with potash an acid salt, which according to Dumas is $C_{40}H_{21}O_{10} + KO$; but which is more probably $C_{40}H_{25}O_9 + KO = 2C_{20}H_{12}O_4 + \left\{ \begin{matrix} KO \\ HO \end{matrix} \right\}$.

The carbohydrogen above mentioned may be supposed to pass into caryophyllic acid by the substitution of 4 eq. oxygen for 4 eq. hydrogen. Thus $2C_{10}H_8 = C_{20}H_{16}$; and $C_{20}H_{16} - H_4 + O_4 = C_{20}H_{12}O_4$.

Alcohol, as above mentioned, extracts from cloves a solid substance, caryophylline, which appears to be closely connected both with the carbohydrogen and with the acid. According to Dumas and Ettling, its formula is $C_{20}H_{16}O_2$, or $C_{10}H_8O$, which is identical with that of camphor; from which, however, it differs in being inodorous, and not volatile without decomposition.

The distilled water of cloves deposits another substance in yellowish pearly scales, to which Bonastre has given the name of Eugénine. The analysis of Dumas gives for it the same formula as for caryophyllic acid.

All these substances require to be further studied.

We now come to those oily acids, which, being solid at ordinary temperatures, are more properly called fatty acids, with which, however, are associated a few that are liquid at the ordinary temperature, but not volatile without decomposition, and which constitute the chief part of the liquid fats, or fat oils. We shall first mention those which belong to the series $(CH)_n + O_4$. The fat acids of this series still partake of the characters of those previously described; for while bu-

tyric and valerianic acids are very fluid, and caprylic, pelargonic, and capric acids are semi-solid, the acids now to be mentioned are solid, but fusible and even volatile without decomposition.

LAURIC ACID.

Syn. Laurostearic Acid.—This acid was discovered by Marsson in laurel berries, which contain, besides a resinous matter and a green fluid fat, a solid tallow or fat, called by him Laurostearine. This is a compound of lauric or laurostearic acid with oxide of glyceryle, or rather with oxide of lipyle, C_3H_2O , which is the half of glycerine $C_6H_7O_5$ minus 3 eq. of water, $= \frac{C_6H_4O_2}{2}$.

Laurostearine is crystallizable and fusible at 112° . When boiled with alkalis it is easily saponified, and the soap, decomposed by an acid, yields lauric acid. This acid crystallizes when melted and allowed to cool, but not from alcohol or ether. It is soluble in alcohol and ether, and fusible at 108° . Its formula is $C_{24}H_{23}O_3, HO$.

According to Sthamer, the seeds called Pichurim beans contain the same fat as the laurel berries. The only difference is that the acid of the beans crystallized readily from alcohol. This was probably owing to its greater purity, for this acid yielded, in the analysis of Sthamer, the same formula as lauric acid.

COCINIC ACID.

Formula of the acid in the salt of silver, $C_{26}H_{25}O_3$.

Formula of the hydrated acid, $C_{26}H_{25}O_3 + HO$. (Bromeis.)

This is the crystallizable acid contained in the butter or fat of the cocoa-nut. This fat is white, of the consistence of lard; melts about 70° , and congeals a little above 60° ; has an unpleasant cheesy smell and taste, and becomes readily rancid. It is distinguished from most fats by its ready solubility in alcohol.

To obtain the acid, the fat is converted into soap by boiling with an alkali, and the soap decomposed by a mineral acid. The fatty acid mixture obtained is subjected to strong pressure to remove the liquid acid, (probably oleic acid,) and the pressed cocinic acid is further purified by a second saponification. The soap is repeatedly dissolved in water and separated by the addition of common salt, by which means it is rendered colourless. It is then decomposed by tartaric acid, and the fatty acid crystallized from alcohol till its melting point becomes constant.

It is snow-white, inodorous, and melts at 95° , congealing into a mass like wax. When melted with oxide of lead, it loses 4 eq. water.

With the alkalies it forms salts which are soaps, like the salts of the more common oily acids. The cocinate of oxide of ethyle is obtained by passing hydrochloric acid gas into a solution of cocinic acid in alcohol, and adding water. It is a colourless mobile liquid, having a pleasant smell of apples. The cocinate of silver is white and insoluble.

MYRISTIC ACID.

Syn. Sericic Acid.—Discovered by Playfair. Formula of the acid in the salts of baryta and potash, $C_{28}H_{27}O_3$. Formula of the crystallized acid, $C_{28}H_{27}O_3 + HO$. (Playfair.)

This acid exists in combination with oxide of glyceryle in the butter of nutmegs, which are the fruit of *Myristica moschata*. This butter is soluble in 4 parts of hot alcohol, and the solution deposits on cooling silky crystals of myristate of oxide of glyceryle (sericine or myristine). From this purified fat the acid is obtained by the usual process for oily acids, as described for the preceding acid. It is purified by repeated crystallization from alcohol or ether.

It forms brilliant white scales of a silky lustre, (hence the name sericic acid,) fusible about 120° , and congealing into a crystalline mass. It is soluble in alcohol and ether, and is decomposed by nitric acid and by heat.

The salts which myristic acid forms with alkalies are distinguished from other soaps by not forming viscid solutions when concentrated, and by not becoming turbid when diluted, as ordinary soaps do. Myristate of oxide of ethyle is a colourless mobile liquid, of sp. gr. 0.864.

Formula, $2\overline{My} + \left\{ \begin{matrix} AeO \\ HO \end{matrix} \right\}$.

Myristate of oxide of glyceryle, or myristine, exists in the butter of nutmegs. It is purified by washing with alcohol, pressure, and solution in hot ether, from which it crystallizes on cooling. According to Playfair, its formula is $C_{118}H_{113}O_{15} = 4(C_{28}H_{27}O_3) + C_6H_5O_3$. This would give for the oxide of glyceryle in this fat the formula $C_6H_5O_3$; whereas, according to Pelouze, oxide of glyceryle is $C_6H_7O_5$. But it is not impossible, as Liebig has suggested, that there may be more than one oxide of glyceryle. According to Lecanu, oxide of glyceryle is $C_6H_6O_4$; and it will be seen that these three formulæ only differ in the proportion of water. Liebig supposes that these different varieties of glycerine may require different quantities of acid for neutralization, just as some acids are monobasic, others polybasic. He con-

siders stearine a compound of 2 at. stearic acid, 1 at. oxide of glyceryle = $C_6H_7O_5$, and 2 at. water; while in sericine, the oxide of glyceryle $C_6H_5O_3$, which contains 2 at. of water less, is combined with 2 at. of acid more, 4 at. in all. It has also been supposed by Liebig that oxide of glyceryle may be = C_3H_2O , called by Berzelius oxide of li-pyle, in which case the formula of myristine may be $\overline{My} + LiO$, or possibly $2(\overline{My}, LiO) + 2(\overline{My}, HO)$. Like all compounds of glyceryle, myristine, when distilled, yields the pungent vapour of the substance formerly mentioned under the name of oxide of acryle or acroleine.

Myristic acid, when heated with potash and a little water, forms a beautiful white soap, which crystallizes out of alcohol. This, as well as the myristate of baryta, is composed according to the general formula $\overline{My}, MO$.

Myristate of silver appears to contain water, a rare occurrence in a salt of silver. If so, its formula is $2(\overline{My}, AgO) + HO$. But it is more probably $\overline{My}, AgO$.

Myristate of lead, like some other salts of lead, when prepared from the acetate, contains acetate of lead. Its formula is $C_{116}H_{111}O_{15}, 7PbO = 4(C_{28}H_{27}O_3, PbO) + (\overline{A}, 3PbO)$.

Playfair, to whom we are indebted for the above and other facts, remarks that myristic acid is not far removed in composition from œnanthic acid. In fact, 2 at. œnanthic acid = $C_{28}H_{26}O_4$ represents 1 at. myristic acid in which 1 eq. of hydrogen has been replaced by 1 eq. of oxygen. It is thus related to œnanthic acid, as hyduret of benzoyle is to benzoic acid, at least as far as the formulæ are concerned; but no conversion of the one into the other has been observed.

Besides myristine, the butter of nutmegs contains a reddish fat and an aromatic volatile oil. The reddish fat, when distilled, yields, among other products, a black fat, soluble in alcohol and ether. These products have not been further examined.

PALMITIC ACID.

Formula of the acid in the salt of silver, $C_{32}H_{31}O_3$. Formula of the hydrated acid, $C_{32}H_{31}O_3 + HO$. (Fremy, Stenhouse.) Discovered by Fremy in palm oil. To obtain it, the oil is saponified by a caustic alkali, and the soap decomposed by an acid. The fatty acid which separates contains some oleic acid, which is removed by solution in alcohol and by pressure.

In appearance the palmitic acid resembles margaric acid, forming

pearly scales. It has also the same melting point, namely, 140° . It is saponified by digestion with the carbonated alkalis. It is partly decomposed by distillation. By chlorine it is acted on in a way similar to valerianic acid, yielding a variety of acid oils, in which the hydrogen is more or less completely replaced by chlorine, and which retain their chlorine in combining with alkalis.

Palmitine, or palmitate of oxide of glyceryle, is the principal solid ingredient of the palm oil or butter. It is purified by pressure, washing with hot alcohol, and, finally, crystallization from hot ether. It is white and crystalline, very sparingly soluble in hot alcohol, but very soluble in hot ether. It melts at 118° , and congeals to a mass like wax, which is friable. According to Stenhouse, its formula is $C_{35}H_{33}O_4$, which would indicate a compound of 1 at. anhydrous palmitic acid, $C_{32}H_{31}O_3$, united to C_3H_2O ; which is the same formula for glycerine as one of those mentioned under the preceding acid as suggested by Liebig, and now called oxide of lipyle. This is possibly derived from ordinary glycerine, $C_6H_7O_5$; for $C_6H_7O_5 - 3HO = C_6H_4O_2 = 2(C_3H_2O)$. Like all the compounds of glycerine, palmitine, when distilled, yields the penetrating vapours of acroleine.

Palmitate of Potash is an acid salt, composed of $\overline{Pa},KO + \overline{Pa}HO + 2aq$. Unlike soaps in general, it forms beautiful crystalline scales, like those of chlorate of potash.

Palmitonic Acid.—This name is given by Schwarz to a new acid, which he obtained from palmitic acid, as manufactured for candles, and bleached by exposure to the air. This acid melts at 124° , and does not crystallize nearly so well as palmitic acid. The potash salt is also amorphous. Its formula is $C_{31}H_{30}O_3,HO$; and it therefore differs from palmitic acid by 1 eq. of CH . The oxygen of the air acts on palmitic acid by converting CH into carbonic acid and water, thus producing the new acid. Palmitonic as well as palmitic acid may be distilled unchanged, if the heat be carefully regulated.

CETYLIC ACID.

Syn. Ethalic Acid.—Composition and formula identical with those of palmitic acid, from which, however, it differs in properties. (Dumas and Stass.) Formed by the action of fused potash on ethal (hydrated oxide of cetylc). It exists in spermaceti, combined with oxide of cetylc, constituting cetine, which is purified spermaceti. Symbol, $\overline{Cet}$.

The formula of ethal is $C_{32}H_{34}O_2$; that of cetylic acid is $C_{32}H_{32}O_4$. The latter is therefore produced from the former, 2 eq. of hydrogen being replaced by 2 eq. of oxygen. The oxygen is derived from the

water of the hydrate of potash; so that 4 eq. of hydrogen are set free in the process, 2 from this source, and 2 from the ethal. To prepare the acid, 1 part of ethal is heated with 6 parts of a mixture of fused potash and quicklime in equal proportions, to the temperature of about 425° . Hydrogen is set free, and cetylate of potash is formed. This salt is converted, by means of chloride of barium, into cetylate of baryta, which is purified from ethal by digestion in ether. The cetylate of baryta is decomposed by diluted hydrochloric acid, when cetylic acid is obtained in the form of a fat, fusible at 130° , volatile, insoluble in water, soluble in alcohol or ether. Cetylic acid, according to L. Smith, is more advantageously prepared from spermaceti (cetine) by the process given under the Hydrated Oxide of Cetylc, p. 1015. Its salts have the general formula $\overline{\text{Cet}},\text{MO}$. They have been little studied.

MARGARIC ACID.

Syn. Margarylic Acid.—Formula of the anhydrous acid, $\text{C}_{34}\text{H}_{33}\text{O}_3$, or $\text{C}_{68}\text{H}_{66}\text{O}_6$. Symb. $\overline{\text{Mr}}$. Formula of the hydrated acid, $\text{C}_{34}\text{H}_{33}\text{O}_3, \text{HO}$; $\text{C}_{68}\text{H}_{66}\text{O}_6 + 2\text{HO}$. (Varrentrapp, Redtenbacher, Bromeis, Stenhouse.) Symb. $\overline{\text{Mr}}, 2\text{HO}$. A bibasic acid? Discovered by Chevreul.

Margaric acid, one of the most widely distributed and most important of the fatty acids, is found in combination with oxide of glycercyle (glycerine, sugar of oils) in several species of animal and vegetable fats and oils, particularly in human fat, in goose fat, and in olive oil, being in these cases mixed or combined with oleate of oxide of glycercyle. The solid fat of butter is pure margarine, and, when purified from the fluid oleine, contains no stearine. (Bromeis.) It is also produced by the action of heat on tallow (stearate of oxide of glycercyle) and on stearic acid, and by the oxidation of stearic acid.

The easiest method of obtaining pure margaric acid is to heat hydrated stearic acid with its own weight of nitric acid for some minutes. The fatty acid which separates on cooling is exposed to pressure to remove oleic acid, and purified by repeated crystallization in alcohol, till its melting point becomes constant. It may also be obtained by decomposing pure margarate of lead or of lime by a diluted mineral acid.

Margaric acid has the aspect of a fat, fusible at 140° , and volatile at a higher temperature. Its solution in alcohol has an acid reaction. From ether or alcohol it crystallizes in pearly scales; hence its name.

With bases it forms two series of salts: *a.* Neutral, the general formula of which is $\overline{\text{Mr}} + 2\text{MO}$; *b.* Acid, the general formula of

which is $\overline{\text{Mr}} + \left\{ \begin{smallmatrix} \text{MO} \\ \text{HO} \end{smallmatrix} \right\}$. (Varrentrapp). $\overline{\text{Mr}}$ is here $\text{C}_{68}\text{H}_{66}\text{O}_6$, and the acid is viewed as bibasic. But if it be considered monobasic, and $\overline{\text{Mr}}$ be $= \text{C}_{34}\text{H}_{33}\text{O}_3$, the formulæ will be $\overline{\text{Mr}} + \text{MO}$ for the neutral, and $\overline{\text{Mr}}, \text{MO} + \overline{\text{Mr}}, \text{HO}$ for the acid series of its salts.

SALTS OF MARGARIC ACID.

Margarate of Oxide of Ethyle.— $\overline{\text{Mr}}, 2\text{AeO}$. (Varrentrapp.) Prepared by the action of hydrochloric acid gas on an alcoholic solution of margaric acid, and purified by washing with boiling water. It has the appearance of a fat, which melts at about 70° .

The *margarates of potash and soda* were formerly obtained pure by the following method, which we owe to Chevreul. The fat of man or of the goose, or olive oil, is saponified by boiling with caustic potash or soda. The soaps obtained are decomposed by a mineral acid; and the fatty acid which separates, a mixture of margaric and oleic acids, is heated with 8 parts of water, and potash or soda added till a clear solution is obtained. This solution is then mixed with 50 times its volume of water, which causes the separation of acid margarate of the alkali in pearly scales. These are again dissolved in 8 parts of water, the solution again rendered clear by potash or soda, and again mixed with 50 volumes of water. This operation is repeated till the salt, when decomposed, yields an acid fusible at 140° . The salt is then free from oleate of potash or soda. The acid margarate of potash is $\overline{\text{Mr}} \left\{ \begin{smallmatrix} \text{KO} \\ \text{HO} \end{smallmatrix} \right\}$. Heated with as much more potash as it already contains, it yields the neutral salt, $\overline{\text{Mr}}, 2\text{KO}$, which is a regular soap, of a rather soft consistence, soluble both in water and alcohol, but which, when mixed with much water, yields free potash and the acid salt, the latter being insoluble. This, and all other salts of margaric acid, however, are much more easily prepared directly with the pure acid, as extracted from butter, and purified from oleic acid till its melting point rises to 140° .

The *margarates of soda*, acid and neutral, are quite analogous to those of potash; but the neutral margarate of soda is a somewhat harder soap.

The margarates of baryta, strontia, and lime are insoluble, white, curdy precipitates. Margarate of lime is easily obtained pure, by dissolving in potash the first half of the products of the distillation of stearic acid, precipitating by chloride of calcium, and boiling the pre-

cipitate repeatedly with ether, to remove margarone and a carbohydrogen with which it is contaminated. The purified salt is employed to yield margaric acid.

With oxide of lead, margaric acid forms a neutral, an acid, and a basic salt, all insoluble. The latter is fusible at 212° , and is a true plaster, as the salts of oxide of lead with oily acids commonly are.

Margarate of Oxide of Glyceryle. *Syn. Margarine.*—This compound is unknown in a state of perfect purity, but is the principal ingredient of human fat and of goose fat, and of butter, combined with the corresponding oleate. It occurs also in a smaller proportion in olive oil, and probably in many other fats and oils. The crystals deposited by a hot alcoholic solution of human fat are a chemical compound of margarate and oleate of glyceryle. (Chevreul.) So also are the crystals which form in olive oil when it is exposed to cold. (Pelouze, Boudet.)

The original analyses of Chevreul, which, however, appear to have been made with a margaric acid not quite free from oleic acid, suggest a somewhat different formula from that given above; but the close relation between margaric and stearic acids renders the formula of Varrentrapp more probable. After describing, therefore, stearic acid, we shall give a connected view of these very interesting acids, as far as our knowledge of them at present extends. Margaric acid is the highest yet known of the series $(CH)_n + O_4$. It will be remembered that this series began with acetic acid which is not oily, $n = 4$, after which came metacetic acid, $n = 6$, which forms the link between acetic and butyric acids. Margaric acid, although a fat, partakes of the characters of the series, for it is volatile without change, a property not found in the fat acids which do not belong to that series. These acids we now proceed to describe.

STEARIC ACID.

Syn. Hypomargarylic Acid.—Discovered in 1811 by Chevreul. Studied by Redtenbacher. Formula of the anhydrous acid, $C_{68}H_{66}O_5$. Symb. $\bar{St}$. Formula of the hydrated acid, $C_{68}H_{66}O_5 + 2HO$. (Redtenbacher.) A bibasic acid?—and one of the most interesting and important of all the oily acids.

It is best obtained from the stearic acid of commerce, which is used as a substitute for wax in making candles. This commercial acid is prepared by saponifying ox or mutton fat by boiling with potash, precipitating by chloride of calcium, and decomposing the stearate of lime thus formed by a mineral acid. The mixture of stearic and oleic acids thus obtained is freed as far as possible from oleic acid by pressure

between warm metallic plates. It thus yields a hard mass like wax. To purify it completely, it is repeatedly crystallized from hot alcohol, till its point of fusion becomes constant at 167° . Stearic acid may also be obtained from the acid stearate of potash, (see that salt,) but still requires to be purified by alcohol, till it acquires the above melting point.

Stearic acid is a firm white solid. When melted, it congeals at 158° into a crystalline mass, which feels greasy, but it is pulverizable, and insoluble in water. From alcohol it is deposited in brilliant pearly scales. In the liquid state, at 170° , its sp. gr. is 0.854; in the solid state it is 1.01. It is very soluble in ether. It burns like wax, with a clear white flame.

When distilled, it is converted into margaric acid and margarone. Heated with nitric acid, it is first converted into margaric acid; and, by the continued action of nitric acid, the latter is converted into succinic and suberic acids.

STEARIC ACID AND BASES.

As a bibasic acid, stearic acid forms two series of salts: *a.* Neutral. Formula, $\overline{\text{St}}, 2\text{MO}$. — *b.* Acid. Formula, $\text{St} \left\{ \begin{smallmatrix} \text{MO} \\ \text{HO} \end{smallmatrix} \right\}$. Stearic acid partially decomposes the alkaline carbonates in the cold, yielding bicarbonate and acid stearate of the alkali. With the aid of heat it expels the carbonic acid entirely, forming a neutral stearate, which is a complete soap, in the case of potash or soda.

Stearate of Ammonia.—Hydrated stearic acid absorbs 2 eq. of ammonia, forming a white inodorous solid. It is soluble in ammonia, but deposits crystals of the acid salt, the formula of which is $\overline{\text{St}}, \text{AdH}_2\text{O}, \text{HO}$. (Chevreul.)

Stearate of Oxide of Ethyle.—*a.* Neutral. $\overline{\text{St}}, 2\text{AeO}$. This is formed, according to Lassaigne, by heating together stearic acid, alcohol, and oil of vitriol. An oily liquid rises to the surface, which solidifies on cooling.—*b.* Acid. $\overline{\text{St}} \left\{ \begin{smallmatrix} \text{AeO} \\ \text{HO} \end{smallmatrix} \right\}$. When hydrochloric acid gas is passed through an alcoholic solution of stearic acid, this compound separates. It resembles wax, and melts between 80° and 90° . It crystallizes from alcohol, and is decomposed by boiling with potash, yielding stearic acid and alcohol. (Redtenbacher.)

Stearate of Oxide of Methyle, neutral, according to Lassaigne, is formed like the neutral compound of ethyle, which it resembles.

Stearate of Oxide of Glyceryle.—This compound, the stearine of Chevreul and Lccanu, is, according to Pelouze and Liebig, an acid salt. Formula, $2\overline{\text{St}} + \text{GlyO} + 2\text{HO}$?. It is the chief ingredient in most kinds of suet or tallow, and is the most important of the fatty bodies.

To obtain pure stearine, mutton suet is melted in the water-bath, mixed with ten parts of ether, and set aside to cool. The crystals which are deposited on cooling are strongly pressed, and washed with cold ether. They are pearly scales, which feel soft, but not greasy; fusible about 140° to 145° ; and congealing to a mass like wax, not crystalline, and easily reduced to powder. It is insoluble in water, soluble in hot alcohol and ether; both of which solvents, on cooling, deposit almost the whole of the stearine. When distilled, it yields the products of the action of heat on stearic acid, which are margaric acid and margarone, besides a carbohydrogen, as well as the products of the distillation of glycerine, particularly acroleine.

Stearine has weak acid properties. By careful management it may be made to combine with potash, forming a compound from which acids separate stearine, and not stearic acid. The probable formula of this compound is $2\text{St} + \text{GlyO} + \left\{ \begin{array}{l} \text{KO} \\ \text{HO} \end{array} \right\}$.

But when stearine is boiled with caustic alkalies, stearate of potash is formed, while hydrated oxide of glyceryle (glycerine) is separated. From 100 parts of stearine Chevreul obtained 102.6 parts of hydrated stearic acid and glycerine together; the glycerine weighed 8 parts. If we admit that 3 at. of water are taken up in this process, two by the half of the stearic acid, and one by the glycerine, 100 parts of stearine should yield, according to the formula of Pelouze and Liebig, 102.3 parts of stearic acid and glycerine; the latter weighing 7.9 parts. This close correspondence not only lends additional probability to the formula given above, but is a wonderful proof of the accuracy of Chevreul in his splendid researches on fatty bodies, made when nothing was known of these compounds.

According to Pelouze and Boudet, the solid part of the butter of cacao is a compound of the above stearate of oxide of glyceryle with the corresponding oleate.

Stearate of Potash.—*a.* Acid. $\overline{\text{St}} \left\{ \begin{array}{l} \text{KO} \\ \text{HO} \end{array} \right\}$. (Chevreul.) To prepare it, the solution of 1 part of the neutral stearate is diluted with 1000 parts of water, when the acid salt separates. It is purified by washing with water and solution in alcohol, from which it crystallizes in pearly scales. One thousand parts of boiling water form with 1 of

this salt a milky solution, which contains neutral stearate dissolved; while the suspended salt is a still more acid compound, $2\overline{\text{St}},\text{KO},3\text{HO}$. Three atoms of acid stearate, $3(\overline{\text{St}},\text{KO},\text{HO})$, produce 1 atom of neutral salt, $\overline{\text{St}},2\text{KO}$; and 1 at. of the new salt, $2\overline{\text{St}}\left\{\begin{smallmatrix}\text{KO} \\ 3\text{HO}\end{smallmatrix}\right\}$. The latter is fusible into an oily liquid, while the original acid salt is only softened by heat. (Chevreul.)

b. Neutral. $\overline{\text{St}},2\text{KO}$. When equal weights of stearic acid and potash are dissolved in 10 parts of hot water, the neutral salt separates on cooling in opaque grains, which are to be squeezed and purified by solution in hot alcohol, from which it crystallizes in shining scales and needles. With 10 parts of cold water, this salt forms an opaque viscid solution. It is soluble in 25 parts of hot water; more soluble in solution of potash. From this latter solution, when hot and saturated, the addition of chloride of potassium separates the salt entirely in the form of an opaque viscid mass, which, on cooling, forms a firm soap. If chloride of sodium be employed, the salt which separates is neutral stearate of soda, which, on cooling, forms a very hard soap.

Neutral stearate of potash, as above described, is resolved by 1000 to 5000 parts of cold water into potash, which remains dissolved, and acid stearate, which separates. (Chevreul.) The neutral salt is soluble in hot alcohol, and on cooling forms a jelly (opodeldoc). It is insoluble in ether.

Stearates of Soda.—*a. Acid.* $\overline{\text{St}},\text{NaO},\text{HO}$. Prepared from the neutral salt like the corresponding salt of potash, which it resembles.—*b. Neutral.* It is prepared like the neutral soap of potash from 20 parts of stearic acid, 13 of soda, and 300 of water. It may be obtained either in crystals from alcohol, or as a hard soap from water by adding chloride of sodium to the hot saturated aqueous solution, an excess of soda being also present. The action of water and alcohol on this soap is much the same as on the neutral salt of potash, only the soda soap is less soluble and less easily decomposed by water, requiring at least 2000 parts.

The *Stearates* of Baryta, Strontia, and Lime are all neutral according to the general formula, $\overline{\text{St}},2\text{MO}$. They are white insoluble precipitates.

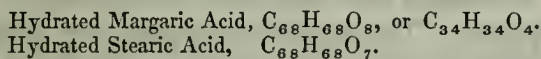
Neutral Stearate of Lead, $\overline{\text{St}},2\text{PbO}$, resembles the preceding.

Basic Stearate of Lead, $\overline{\text{St}},4\text{PbO}$, prepared by boiling stearic acid with subacetate of lead, is a transparent soap or plaster fusible at 212° .

Acid Stearate of Lead is formed by melting 100 parts of stearic acid with 21 of oxide of lead. It is also a transparent soap or plaster, fusible at 212° .

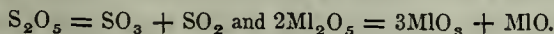
ON THE COMPOSITION OF STEARIC AND MARGARIC ACIDS.

As already mentioned, the recent researches of Varrentrapp, Redtenbacher, Bromeis, and Stenhouse lead to the following formulæ for the two hydrated acids:—



Margaric acid forms with oxide of silver a salt, the formula of which is $C_{34}H_{33}O_3, AgO$, so that the hydrate might be supposed to be $C_{34}H_{33}O_3, HO$; but, as it forms two series of salts, in one of which only half this quantity of water is replaced by a base, we are induced to consider it as a bibasic acid, $C_{68}H_{66}O_6, 2HO$. The margarate of silver will then be $C_{68}H_{66}O_6, 2AgO$. Taking this view, and comparing it with stearic acid, we find it to contain 1 atom of oxygen more than that acid, while the carbon and hydrogen remain exactly in the same proportion. If we now call this compound of carbon and hydrogen margaryle $= C_{34}H_{33} = Ml$, we find that anhydrous margaric acid $= 2(MlO_3) = Ml_2O_6$, and anhydrous stearic acid $= Ml_2O_5$. Again, comparing 1 atom $= \frac{1}{2}$ equivalent of margaric acid $= MlO_3$, with 1 equivalent of stearic acid, we find them to bear the same relation to each other as sulphuric and hyposulphuric acids, SO_3 and S_2O_5 . The only difference is, that, while sulphuric acid is monobasic as well as hyposulphuric acid, the two acids of margaryle, which may be called margarylic and hypomargarylic acids, are both bibasic.

If this be really the relation between margaric and stearic acids, if they be different oxides of the same radical, we should expect to be able to convert stearic (hypomargarylic) acid into margarylic acid by oxidizing agents. This is in fact the case, as formerly described. The change is effected by the action not only of nitric acid, but of a mixture of sulphuric acid and bichromate of potash. Moreover, just as hyposulphuric acid S_2O_5 , is resolved by heat into sulphurous acid SO_2 , and sulphuric acid SO_3 , so hypomargarylic (stearic) acid, when distilled, is resolved into oxide of margaryle (margarone) MlO , and margarylic acid MlO_3 ; that is, in both cases, one portion yields oxygen to another; thus,



All these facts render it almost certain that the above is a true account of the constitution of margaric and stearic acids.

The original analyses of Chevreul, indeed, gave for anhydrous margaric acid the formula $C_{70}H_{65}O_3$, or the half of this, $= \frac{C_{70}H_{65}O_3}{2}$; and for anhydrous stearic acid the formula $C_{70}H_{67}O_5$. But not only was the method then used for determining the atomic weights of the acids inferior to that now employed, but the acids themselves were possibly not absolutely pure. It is worthy of remark, however, that Berzelius, observing that in these acids, according to Chevreul, the same quantity of carbon, 70 atoms, was combined with 3 and 5 atoms of oxygen, was the first to suggest that they were most probably oxides of the same carbohydrogen. This suggestion appears now to be established, and is only another instance of the profound sagacity of Berzelius.

It should also be mentioned here, that five careful analyses of stearine, (acid stearate of oxide of glyceryle,) by Pelouze and Liebig, gave the following results:—

Carbon . .	75.981 to 76.600 per cent.
Hydrogen . .	12.240 to 12.170 per cent.
Oxygen . .	21.779 to 21.330 per cent.

Adopting for stearic acid the formula of Chevreul, and for oxide of glyceryle that of Pelouze, these numbers correspond to the formula $2\text{St}, \text{GlyO}, 2\text{HO}$, which has been given above. But if we take for stearic acid the formula of Redtenbacher, and if we substitute for oxide of glyceryle the formula C_3H_2O , (oxide of lipyle,) then the formula most nearly agreeing with the numbers will be $\text{St}, \text{LiO}, 2\text{HO}$. The former gives $C_{146}H_{143}O_{17}$, the latter $C_{71}H_{70}O_8$. The former would give

Carbon	76.21	the latter,	Carbon	76.43.
Hydrogen	12.18	„	Hydrogen	12.30.

Both are obviously near the truth; but, as long as there is any doubt as to the composition of oxide of glyceryle, or, rather, as to the question, whether the true base of the fat oils be oxide of glyceryle $C_6H_7O_5$, or oxide of lipyle C_3H_2O , the exact composition of stearine cannot be satisfactorily determined. It will be remembered, that, if we admit oxide of lipyle to be the true base, 2 eq. of it in separating will take up 4 eq. of water, yielding glycerine (hydrated oxide of glyceryle), $C_8H_8O_6$; for $2(C_3H_2O) + 4HO = C_6H_8O_6$. It is, therefore, very doubtful if oxide of glyceryle be really present in stearine. Moreover, in bodies of so high atomic weights, a difference of 1, 2, or even 3 eq. of hydrogen, oxygen, or water, will not affect the numerical results beyond the limits of the unavoidable errors of experiment. Notwithstanding the improvements which have been introduced into organic analysis, and the progress which has been made in the study of these substances, the results obtained by Chevreul in his masterly

researches have undergone but little modification, except in the interpretation of the analytical part of his immortal work; the numerical results being correct in a degree quite wonderful, when we consider the difficulties then attending organic analysis; and, above all, that the whole subject of the fatty bodies was then untouched, inasmuch that, till Chevreul discovered them, the oily acids were unknown, and the nature of soaps altogether misunderstood.

ACTION OF HEAT ON STEARIC AND MARGARIC ACIDS.

When these acids are distilled, they yield a product, the melting point of which is almost the same as that of the acids; and hence they were formerly supposed to distil nearly unchanged, although Chevreul had observed that the product was no longer entirely soluble in alkalies.

Redtenbacher and Varrentrapp have lately examined this subject minutely, with the following results.

Pure stearic acid, melting at 158° , yields a solid product, which melts at about 156° . This is a mixture of pure margaric acid, melting at 140° , and a neutral crystalline fat melting at 190° , besides a liquid substance. This mixture is dissolved by potash, forming a milky liquid, which is precipitated by chloride of calcium. The precipitate, boiled with ether, leaves pure margarate of lime; while the ether being evaporated leaves the solid and liquid neutral compounds above mentioned. The former is margarone; the latter a carbohydrogen.

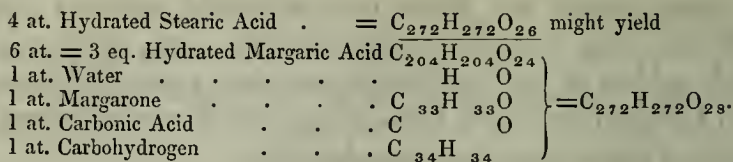
When stearic acid is distilled with one-quarter its weight of quicklime, carbonate of lime is left in the retort, while margarone and the carbohydrogen distil over.

It is particularly to be observed, that the products of the distillation of stearic and margaric acids contain no substance soluble in water, and particularly no *sebacic acid*.

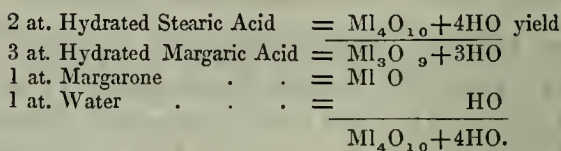
Margarone.—Discovered by Bussy. Obtained by distilling stearic or margaric acids with or without lime. It is purified by crystallization from ether.

Margarone is a white, crystalline, friable fat, fusible generally at 190° , but sometimes at 200° and upwards, indicating the existence of more than one compound, the composition of which, however, seems to be nearly uniform. The analyses of margarone by Bussy, Redtenbacher, and Varrentrapp indicate two formulæ, between which it is difficult to decide. The first is $C_{33}H_{33}O$, which may arise from anhydrous margaric acid by the loss of 1 at. carbonic acid: $C_{34}H_{33}O_3 - CO_2$

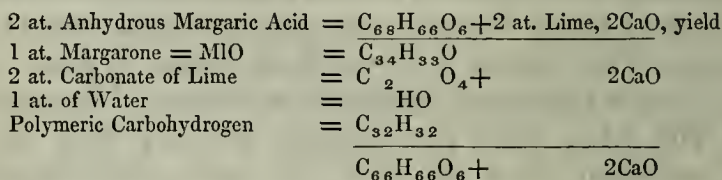
$= C_{33}H_{33}O$. This would account for the agency of lime in its production. Again,



On the other hand, if we adopt for margarone the formula $C_{34}H_{33}O = MlO$, then



From the margarone the carbohydrogen may be formed along with carbonic acid and carbon; for 2 at. margarone $= C_{68}H_{66}O_2 = C_{66}H_{66} + CO_2 + C$. That this does happen is indicated by the deposition of carbon. The formation of margarone from margaric acid and lime is also easily explained.



From stearic acid with lime Redtenbacher obtained a compound like margarone, but composed of $C_{46}H_{45}O$. This may be a compound of oxide of margaryle with a carbohydrogen, $C_{34}H_{33}O + C_{12}H_{12} = C_{46}H_{45}O$.

A similar compound, discovered by Bussy, and called by him stea-
rone, is $C_{68}H_{66}O$. It is possibly Ml_2O , a suboxide of margaryle.

In all these researches the carbohydrogens were found to contain equal equivalents of hydrogen and carbon; but as they form no combinations from which their atomic weights can be deduced, it is impossible to say whether they may contain one equivalent of each element, or a certain number of CH in one atom. In fact, there appears to be an unlimited number of such carbohydrogens, agreeing in relative proportions, but differing in the absolute quantity of their elements; in other words, in their atomic weight.

PRODUCTS OF THE ACTION OF NITRIC ACID ON STEARIC AND MARGARIC ACIDS.

SUBERIC AND SUCCINIC ACID.

If stearic acid be heated with an equal weight of nitric acid, sp. gr. 1.285, for a few minutes, it is entirely converted into margaric acid, while the nitric acid contains no foreign substance. But if the action be continued, the nitric acid being occasionally renewed, the margaric acid is by degrees entirely decomposed, and the liquid on cooling deposits nothing. If evaporated to one-half, it deposits *Suberic acid*, and contains succinic acid, and an oily liquid soluble in nitric acid. (Bromeis.)

Suberic Acid.—Formula of the anhydrous acid, $C_8H_6O_3$. Symbol, $\overline{Su}$. Formula of the crystallized acid, $C_8H_6O_3.HO$. Symbol, $\overline{Su}.HO$. Discovered by Brugnatelli as the product of the oxidation of cork by nitric acid; by Laurent as a product of the action of nitric acid on oleic acid and olive oil; and by Bromeis as a product of the action of nitric acid on stearic and margaric acids.

The solution of margaric acid in nitric acid, after long boiling, is evaporated to one-half, when it deposits a quantity of crystals. These are washed with cold water, and purified by crystallization. They are hydrated suberic acid. From cork it is obtained by a similar process. It forms a white crystalline powder; fusible, if moist, at 130° , and if dry at 238° . In a higher temperature it sublimes, condensing into an oily liquid, which congeals into long needles. It is easily soluble in hot water, alcohol, and ether.

In the salts of suberic acid, 1 at. of basic water is replaced by 1 at. of base. Suberate of oxide of ethyle is a fragrant oily liquid, $\overline{Su}, AeO$. The alkaline suberates are soluble. Those of baryta, strontia, lime, and silver are neutral and insoluble. With oxide of lead suberic acid forms a neutral salt $\overline{Su}, PbO$, and a basic salt $\overline{Su}, 3PbO$. (Bromeis.)

When suberate of lime, baryta, or strontia is distilled with excess of base, there is obtained, among other products, a liquid boiling at 367° , which absorbs oxygen from the air or from nitric acid, and is converted into suberic acid. According to Boussingault, its formula is C_8H_7O . It may be considered as a hyduret of suberyle, $C_8H_6O + H$, analogous to hyduret of benzoyle. It may also be the oxide of another radical, C_8H_7 .

Succinic Acid.—Formula of the anhydrous acid, $C_4H_2O_3$. Symb. $\bar{S}$. Formula of the sublimed acid, $C_8H_5O_7 = 2\bar{S} + HO$. Formula of the hydrated acid, $C_4H_2O_3.HO = \bar{S}.HO$.

Succinic acid exists ready formed in amber (succinum), and in the resins of certain coniferæ. (Unverdorben, Lecanu, and Serbat.) It is also one of the products of the oxidation of stearic and margaric acids, and in general of all fatty bodies; also of wax and spermaceti. It has also been obtained by Piria as a product of the decomposition of asparagine, and seems to be of very frequent occurrence.

To obtain it, the products of the distillation of amber are filtered through moistened paper, to separate empyreumatic oil; the filtered liquid is evaporated, and the crystals which it deposits are purified by sublimation. To prepare it from the oily acids, the mother liquid of the suberic acid, as above described, is evaporated, and the crystals which separate are purified from suberic acid by cold ether, which dissolves the latter.

Hydrated succinic acid crystallizes in colourless scales or prisms, of sp. gr. 1.55, which are entirely volatile. The sublimed acid contains only half the quantity of water, and by repeated sublimation it may be rendered at last anhydrous.

Anhydrous sulphuric acid acts on it, producing a new acid, in which 2 at. of sulphuric acid and 1 at. of hydrated succinic acid combine, the elements of 1 at. of water becoming basic. Its probable formula is $C_4H_2S_2O_9.HO$.

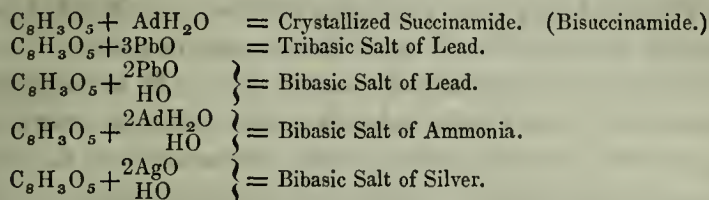
Succinic acid, contaminated with the empyreumatic oil formed in the distillation, has been, and still is occasionally, used in medicine. The oil is the active ingredient, probably from containing kreosote.

Succinamide.—This substance is formed by the action of aqua ammoniæ on succinate of oxide of ethyle. It is a crystalline solid. Formula, $C_4H_2O_2 + NH_2 = \bar{S}.Ad$. It differs from succinate of oxide of ammonium by 2 at. of water. (Liebig.)

Bisuccinamide.—When anhydrous succinic acid is heated in dry ammonia, a crystalline volatile body is obtained, which D'Arcet calls bisuccinamide. Its formula is $C_8H_3O_4 + NH_2 = (C_8H_4O_6 + NH_3) - 2HO = (2\bar{S} + AdH) - 2HO$. When bisuccinamide is dissolved in water, the solution yields crystals, the formula of which is $C_8H_7NO_6 = (C_8H_4O_6 + NH_3)$; that is, anhydrous bisuccinate of ammonia. But it does not appear to be that salt, but rather bisuccinamide with 2 at. water (of crystallization?). (D'Arcet.)

Some uncertainty exists in regard to the true constitution of succinic acid and its salts. According to the prevailing view, the salts of

succinic acid have the general formula $C_4H_2O_3 + MO$. But Fehling, by recent researches, has rendered it probable that succinic acid is a tribasic acid, and that the hydrated acid is $C_8H_3O_5 + 3HO$. According to this chemist, the following is a view of the succinates:—



The later researches of Döpping, however, tend to establish the view that succinic acid is monobasic, and its formula $C_4H_2O_3.HO$. The simplicity of this, the original, formula, is consistent with its frequent occurrence as a product of oxidation.

All the succinates are decomposed by distillation.

Succinate of Ammonia.—The solution of the neutral salt is used in analysis to precipitate peroxide of iron. It deposits crystals, which are permanent in the air, and volatile, while the liquid becomes acid. An impure solution was formerly used in medicine.

Succinate of Oxide of Ethyle is an oily liquid, of sp. gr. 1.036 in the liquid state, and 6.06 in the state of vapour. It boils at 417° . With aqua ammoniæ it forms a crystalline substance, apparently analogous to oxamethane. (D'Arcet.) The remaining succinates are of little importance. Those of lead and silver are white and insoluble.

Succinone.—When succinic acid is distilled with lime, an oily liquid is obtained, to which D'Arcet has given the name of Succinone. As his analyses of it do not agree together, its formula must be considered unknown.

APPENDIX TO SUCCINIC ACID.

AMBER.

The origin of this well-known substance is still doubtful. It is commonly viewed as having been originally a vegetable balsam or resin, altered by time. But the production of succinic acid from oily acids renders it probable that amber is a product of the decay of wax, or of some other substance allied to the fats or fixed oils.

It is found on the coast of Prussia, partly in beds of fossil wood or brown coal, partly on the shore, and at the bottom of the sea. After storms it is found on the shore among the sea-weeds torn up by the agitation of the water. To judge by the remains of vegetables which accompany it, it is the produce of extinct coniferæ, and it frequently

contains insects, almost always of extinct species. One species is said to exist at the present day in America, and species allied to others occur in Brazil and New Holland. Amber occurs sparingly in other parts of Europe, as in the neighbourhood of London and Paris, Sweden, Poland, Italy, Spain; and also in Siberia and North America; but generally in beds of fossil wood, brown coal, or coal.

Amber occurs in fragments of various sizes. It is transparent or translucent, hard, brittle, of a paler or darker yellow or brown colour, of sp. gr. 1.065 to 1.07; tasteless and inodorous, but acquiring an aromatic smell when heated. It becomes highly electric by rubbing, and was the first substance in which this property was observed; hence the term electricity (from *ηλεκτρον*, amber). It melts at about 550° , but is partially decomposed at that temperature. It is insoluble in water, partially soluble in alcohol.

Amber, according to Berzelius, contains succinic acid, a volatile oil, two resins soluble in alcohol and ether, and a bituminous mass insoluble in all menstrua. This last constitutes more than four-fifths of the amber. According to Hünefeldt, hydrochloric acid extracts from amber, besides succinic acid, another acid, very similar to mellitic acid. When amber is distilled, it yields succinic acid, and a volatile oil (oil of amber); while the bituminous residue, dissolved in a mixture of linseed oil and oil of turpentine, forms amber varnish. According to Vogel, a yellowish substance is found along with the acid and oil, which he calls camphor of amber.

The oil of amber is a mobile liquid, of a penetrating smell. It is an ingredient of Eau de Luce, along with alcohol and ammonia, and is used as a stimulating essence in cases of fainting. This oil, when acted on by nitric acid, yields an orange-coloured resinous mass, with a strong musky smell (artificial musk).

OLEIC ACID.

Formula of the acid in the salt of baryta, $C_{36}H_{33}O_3$; of the hydrated acid, $C_{36}H_{33}O_3.HO$. (Gottlieb.) Symbol, $\overline{Ol}, HO$.

This acid was discovered by Chevreul, and was subsequently examined by Laurent and by Varrentrapp. Bromeis studied the oleic acid of butter, and considered it as distinct from that of fat or of olive and almond oil. But the formula of the acid remained doubtful, until the very recent researches of Gottlieb proved that the oleic acid of all the above fats and fat oils was essentially the same, that it is extremely prone to undergo oxidation, as indeed all previous observers had remarked, and that, when perfectly purified, its formula was that

above given. The oleic acid analyzed by Chevreul, Varrentrapp, Laurent, and Bromeis, was shewn by Gottlieb to have contained, besides the pure acid, some of the products of its oxidation, for which reason their analyses could not yield the true formula.

Oleic acid, in combination with oxide of glyceryle, or rather with oxide of lipyle, occurs as oleine, that portion, namely, of the fat of man, of the ox, sheep, pig, or goose, of butter, as well as other animal fats, which is liquid at the ordinary temperatures. In these it forms but a small proportion, but in olive oil, almond oil, and other vegetable fat (not drying) oils, oleine is the chief constituent. It is probable that the liquid animal oils, such as whale and seal oil, cod's liver oil, &c., are also chiefly composed of oleine. Oleic acid is therefore of equal importance with any of the fatty acids.

To obtain oleic acid, almond oil must be preferred, as containing more of it than olive oil, or the fluid portion of animal fats. The drying oils, according to Redtenbacher, contain a distinct acid.

Oil of almonds is saponified, and the soap decomposed by an acid. The resulting oily acid is digested in the water-bath for several hours with half its weight of oxide of lead. The mixture is then agitated with twice its volume of ether, and left for twenty-four hours. The ether dissolves acid oleate of lead, leaving undissolved margarate of lead. The clear ethereal solution is now mixed with diluted hydrochloric acid, when the oleic acid is separated, and rises to the surface dissolved in ether. The ether is removed by gentle evaporation, and the oleic acid again saponified by soda. The soap is now purified by being repeatedly dissolved in solution of soda, and separated by the addition of common salt, by which means it may be rendered colourless, or nearly so. The purified soap yields oleic acid hardly coloured, which is washed with water to remove free mineral acid, and deprived of water by the heat of the water-bath.

The acid thus obtained, however, is not pure, being contaminated by products formed by the oxygen of the air, which oleic acid readily absorbs. It may be purified as follows. When exposed to a cold of about 20° F. it congeals to a crystalline mass. The crystals are the pure acid, and the impure fluid portions are separated by pressing it between folds of bibulous paper in small portions and at a lower temperature. The acid thus pressed is again melted, and when it has congealed again subjected to pressure. By repeating this process it becomes whiter and more brilliant. It is now melted, mixed with a little alcohol, and exposed to cold, when the pure acid is deposited in beautiful snow-white needles, which are once more pressed. It is now dried in a current of carbonic acid gas, and when its point of

fusion becomes stationary at 57° it is pure. If it melts at a lower temperature, it must be again crystallized and pressed. This method only applies to such oleic acid as readily congeals into a mass. It is often found naturally associated with so much of the products of its oxidation besides what is formed during the process, that even at 7° it does not congeal. In that case it is purified in a different way, which applies also to the less impure varieties.

The oleic acid is mixed with an excess of ammonia, and chloride of barium is added, by which means insoluble oleate of baryta is formed. This is dried and boiled with repeated portions of alcohol of medium strength, which dissolves by degrees the pure oleate, and on cooling deposits it in small scales. These are purified by re-crystallization, decomposed by tartaric acid, and the oleic acid which separates washed with water, and dried as before, in a current of carbonic acid gas.

Pure oleic acid is, at temperatures above 57°, a perfectly clear colourless fluid of oily consistence, inodorous and tasteless. It does not redden litmus, even when dissolved in alcohol. When once-melted, it does not solidify till it has been cooled down to 39° or 40°, but when solid it does not entirely melt till the temperature reaches 57°. Below 39° it is very hard. It is insoluble in water, soluble in alcohol and ether, and miscible with oils and fats.

When exposed to the air, it rapidly absorbs oxygen, especially at temperatures above 60°, producing, among other products, a brown substance which colours the acid. At the same time it acquires a disagreeable rancid smell.

SALTS OF OLEIC ACID.

Oleic acid is monobasic; it is a very weak acid, and it is very difficult to obtain neutral salts of it with the alkalies. Gottlieb analyzed the oleates of baryta and lead, and found both to be anhydrous, of the general formula, $\bar{O}l + MO$. The oleate of oxide of ethyle is described by Laurent as a tasteless and inodorous, oily, volatile liquid, but its purity is doubtful.

Oleate of oxide of glyceryle, or *oleine*, is the liquid constituent of the fats and fat oils. It is not known in a state of purity. The oleine of drying oils contains a different acid.

The oleates of potash and soda are soft soaps. Oleate of lead has the properties of plaster; that is, it melts easily, and is brittle when cold.

As all the oleates analyzed by Chevreul and Varrentrapp were prepared with an impure acid, it is unnecessary to give their results.

ACTION OF HEAT ON OLEIC ACID.

When oleic acid is heated, it boils at a high temperature, and is thereby decomposed, yielding solid, liquid, and gaseous products. The gaseous products are carbonic acid and carburetted hydrogen. The liquid portion contains a little undecomposed oleic acid, with several liquid carbohydrogens, the boiling point of which varies from 320° to 526° , and a considerable quantity of capric and caprylic acids, with traces of valerianic and butyric acids. The solid product, which is most abundant in the first stage of the distillation, is a new acid discovered by Thénard, and called by him Sebacic acid. This acid is a characteristic product of the distillation of oleic acid from every source, including that from drying oils, and of all fats containing a liquid acid.

SEBACIC ACID.

Formula of the anhydrous acid, $C_{10}H_{18}O_2$. Formula of the hydrated acid, $C_{10}H_{18}O_3$, $HO = \overline{Sb}, HO$. (Dumas, Redtenbacher.)

To obtain it, the whole liquid and solid products of the distillation of oleic acid, oleine, oils, or fats, are boiled with water as long as that liquid deposits anything on cooling. The crystals are washed with cold water, and crystallized from hot water till they become colourless, and free from empyreumatic smell.

Hydrated sebacic acid forms light, white, pearly scales, very like benzoic acid. They melt at 260° to an oily liquid; and at a higher temperature sublime unchanged. It is sparingly soluble in cold water; very soluble in hot water, alcohol, and ether.

SALTS OF SEBACIC ACID.

The cold aqueous solution of sebacic acid causes a white precipitate in the salts of lead or silver. The general formula of the sebrates is $\overline{Sb}, MO$.

The *Sebrates of Potash, Soda, and Ammonia* are very soluble and crystallizable. Their solutions precipitate the salts of lime, forming sebate of lime. $\overline{Sb}, CaO$. (Redtenbacher.)

Sebate of Silver, $\overline{Sb}, AgO$, is a white, curdy precipitate, which, when heated, leaves 51.64 p. c. of metal, and yields a sublimate resembling sebacic acid.

Sebate of Oxide of Ethyle. $\overline{Sb}, AeO$. Prepared like the ethers of

the oily acids generally, by passing hydrochloric acid gas through a solution of the acid in alcohol, and adding water, which separates the new compound. A mobile oily liquid, having a fragrant smell of pine-apples; crystallizable at 16° , and volatile at a temperature above 212° .

The presence of sebacic acid among the products of the distillation of any oil or fatty substance may be considered as positive proof of the presence in that oil or fat of oleic acid, or of a liquid acid closely analogous. Even the drying oils, although the oleic acid they contain appears to be distinct, yield sebacic acid when distilled; while, on the other hand, those oily acids which are solid at ordinary temperatures, such as stearic, margaric, or myristic acids, do not yield the smallest trace of sebacic acid. To ascertain, then, whether an oil, a fat, or an oily acid, contains oleic acid under any of its forms, distil a small portion of it, and boil the product with water. If the filtered liquid deposit crystals on cooling, then oleic acid has been present in considerable quantity. If, again, the liquid deposit nothing, but has acquired the property of precipitating the salts of lead, oleic acid has been present in smaller quantity. But if the water have dissolved nothing, no oleic acid has been present. This is a test of great delicacy, for which we are indebted to Liebig and Redtenbacher.

ACTION OF NITROUS AND NITRIC ACIDS ON OLEIC ACID.

1. *Action of Nitrate of Mercury, or of Nitrous Acid.*

By the action of nitrate of mercury, and more especially by that of nitrous acid, oleic acid is converted into a new acid, solid at ordinary temperatures, to which the name of Elaidic acid has been given. (Poutet, Boudet. See below, *Action of Nitric and Nitrous Acid on Oils.*)

Elaidic Acid.—To prepare it, a current of nitrous acid, as disengaged from a mixture of starch and nitric acid by heat, is passed for four or five minutes through pure oleic acid at a low temperature. After a short time the liquid congeals into a crystalline mass. This is washed with hot water to remove nitric acid, and then dissolved in its own volume of hot alcohol. On standing, this solution forms a semi-solid mass of crystalline scales, which are purified by pressure and re-crystallization. (Meyer.)

Hydrated elaidic acid, thus prepared, resembles sublimed benzoic acid. It melts at 113° ; is extremely soluble in alcohol, less so in ether, insoluble in water. When distilled, a great part passes over

unchanged; but the product, when boiled with water, yields a solution which precipitates the salts of lead and silver, but deposits no crystals. (Meyer.) It contains no capric or caprylic acid. (Gottlieb.)

Gottlieb has shewn that elaidic acid is isomeric with oleic acid, so that the nitrous or hyponitrous acid would seem to act merely by causing a new arrangement of the particles, as when hydrobenzamide is converted into amarine by contact with boiling potash. Ammonia is, however, formed in the process; but the effect is produced by so small a quantity of nitrous acid, that it is difficult to see how that change should operate. Gottlieb found that a small quantity of freshly-prepared elaidic acid, well washed to remove nitrous acid, and then added to a large quantity of oleic acid, gradually converts the whole mass into elaidic acid. On the whole, the production of elaidic acid, which has been in vain attempted by any other means than nitrous acid, coupled with the apparently well established fact of its isomerism with oleic acid, from which it chiefly differs in its point of fusion and its crystalline form, must be regarded as one of the most curious and interesting phenomena of chemistry.

SALTS OF ELAIDIC ACID.

Elaidic acid is a much stronger acid than oleic acid, and decomposes the alkaline carbonates, forming salts which, with 6 to 8 parts of water, yield strong soapy solutions.

Neutral Elaidate of Soda is soluble in alcohol, and crystallizes like the acid. Its solution in water, when diluted, deposits an acid salt, like stearate and margarate of soda.

Elaidate of Silver is a white curdy soap, which may be obtained in crystals from its solution in aqua ammoniæ.

Elaidates of Lead and Baryta are both white and insoluble.

Elaidate of Oxide of Ethyle, prepared by the same process as the other fatty ethers, is an oily liquid, which is decomposed by alkalies. (Laurent, Meyer.)

Elaidate of Oxide of Glyceryle. Syn. Elaidine.—This is the compound produced when oleine (oleate of oxide of glyceryle) is acted on by nitrous acid or nitrate of mercury. (See *Action of Nitrous Acid on Oils and Fats.*)

2. Oxidation of Oleic Acid by Nitric Acid.

The action of colourless nitric acid on oleic acid has been studied by Laurent, who has discovered among the products a series of new

acids, of which one alone, namely, suberic acid, was previously known to chemists. Bromeis has recently repeated his experiments, and confirmed most of his results. As the experiments of both, however, were made on impure oleic acid, containing margaric, and perhaps stearic acid, it is impossible at present to ascribe the origin of all these new compounds to the oleic acid alone. Redtenbacher has since studied the more volatile products of this oxidation, and has found among them no less than nine of the acids belonging to the series of which the formula is $(CH)_n + O_4$.

In this action, nitric acid of sp. gr. 1.42, previously diluted with its volume of water, is employed. If concentrated, the action is almost explosive. Even with the diluted acid it is at first very violent, but afterwards becomes regular and moderate; and with the aid of heat, and a proper supply of nitric acid, the oleic acid is at last entirely dissolved. The vapours of nitric and nitrous acids, which distil over during the process, carry with them a small quantity of an oily fluid, which attacks the organs of respiration, having a most pungent smell.

The solution when completed, and when margaric acid is no longer deposited on cooling, contains the following acids: suberic acid; azelaic acid; pimelic acid; adipic acid; lipic acid; and an oil soluble in nitric acid. Suberic acid is the most abundant product.

The acid solution is evaporated to one-half, and on cooling deposits a mass of crystals, which are placed to drain in a funnel stopped with asbestos, and washed with cold water. They are suberic acid. When dissolved in hot water, there generally separates an oil or fat, soluble in nitric acid, insoluble in water. When purified by crystallization from alcohol, it forms an oily acid, fusible at 86° , and soluble in alkalis with a blood-red colour.

According to Bromeis, the suberic acid thus obtained is pure; but Laurent found it contaminated with *azelaic acid*, which resembles it in appearance, but may be separated by ether, in which the latter is very soluble. The formula of azelaic acid, according to Laurent, is $C_{10}H_8O_4.HO$; differing, he says, from suberic acid by containing 1 at. of oxygen and 1 at. of hydrogen more. But the formula of suberic acid is $C_8H_6O_3.HO$, so that the difference is 2 at. of carbon, 2 at. of hydrogen, and 1 at. of oxygen. Moreover, the supposed azelaic acid was not free from suberic acid; its existence, therefore, is at present doubtful.

Pimelic Acid.—Formula, $C_7H_5O_3.HO$. (Laurent, Bromeis.) The liquid which has deposited the suberic acid is further evaporated, and allowed to stand for some time, when it deposits more suberic acid

in light soft crystals, and pimelic acid in hard crystalline grains. These are first washed with cold water and cold alcohol, which remove most of the suberic acid, and purified by repeated solution in hot water and crystallization. It melts at 273° , and at a higher temperature sublimes in fine pearly scales.

Pimelate of Silver, $C_7H_5O_3, AgO$, is white and insoluble.

Adipic and Lipic Acids.—The mother liquid of the preceding acids is very gently evaporated, and set aside for some days. Crystals are deposited, and the liquid remaining is treated in the same way as long as it yields any crystals. The crystals are collected and purified by solution in hot water, when some of the oil formerly mentioned separates. On cooling, the solution deposits brownish crystals of adipic and lipic acids. They are dissolved in ether, and the solution allowed to evaporate to one-half. Crystals are formed, and the mother liquid, by further evaporation, yields more. The two portions are separately boiled with alcohol, and there is obtained on the one hand adipic acid in rounded grains, and lipic acid in fine long plates. Both are purified by re-crystallization.

Adipic Acid forms round or hemispherical radiated masses, of a brownish colour, very soluble in hot water. It melts at 266° , and may be sublimed unaltered. All its salts, except the adipate of silver, seem to be soluble. According to Laurent, the anhydrous acid is $C_6H_4O_3$, and the hydrate, $C_6H_4O_3, HO$. According to Brömeis, the acid melts at 293° , and its formula is $C_{14}H_9O_7, 2HO$; being thus a bibasic acid, derived from 2 at. of pimelic acid by the replacement of 1 eq. hydrogen by 1 eq. oxygen. The acids analyzed by Laurent and Brömeis may really be distinct, although in most properties they agree.

Lipic Acid crystallizes in long plates, and from alcohol the crystals are particularly fine. It is more soluble in water than adipic acid; and resembles oxalic acid, of which latter, however, no trace is formed in the process. It is fusible at 290° , and sublimes without change in crystals. Formula, $C_5H_3O_4, HO$. (Laurent.)

There generally remains more or less of an oily liquid on the surface of the nitric acid with which oleic acid has been boiled, till, with an excess of acid, no further action is observed. According to Laurent, if this liquid be boiled with alcohol and sulphuric acid, it yields an ether, which he considers to be a compound of oxide of ethyle with another new acid, *Azoleic acid*. By decomposing the ether, he obtained the acid as an oily liquid, the formula of which he considers to be $C_{13}H_{13}O_4$. But, as there is no evidence of its purity, its existence and formula as a separate acid are alike doubtful. According to Brömeis, the oily liquid above mentioned contains several oily acids;

one of which, when the oil is digested with alcohol, readily forms an ether, which seems to be butyrate of oxide of ethyle.

Laurent states, that, when equal weights of oleic acid and nitric acid are heated together, and the residue well washed and treated with alcohol, œnanthic ether is obtained, indicating the formation of œnanthic acid. But, according to Bromeis, the ether thus obtained has not the composition of œnanthic ether; and although its smell is similar, this property may belong to butyric ether, and the ethers of other fatty acids. As butyric and pimelic acids agree in composition, except that the former contains 1 eq. hydrogen more, the occurrence of butyric acid is more probable. We shall see presently that butyric acid is really formed in this process.

The acid liquid which has deposited the pimelic, adipic, and lipic acids, still contains a very soluble acid, not further examined.

Redtenbacher has found, among the volatile products of the oxidation of oleic acid (impure) by nitric acid, the following acids, all belonging to the series $(CH)_n + O_4$:—1. Acetic acid, $n=4$; 2. Met-acetonic acid, $n=6$; 3. Butyric acid, $n=8$; 4. Valerianic acid, $n=10$; 5. Caproic acid, $n=12$; 6. Œnanthylic acid, $n=14$; 7. Caprylic acid, $n=16$; 8. Pelargonic acid, $n=18$; 9. Capric acid, $n=20$.

This very interesting result renders it probable that in plants and animals the volatile oily acids are derived from oleic acid. It is, at least, very remarkable that these acids always accompany oleic acid. They are probably combined with oxide of lipyle, yielding neutral oils, such as butyrine, caproine, or caprine; and, as these compounds usually possess a peculiar odour, varying with the acid, it seems probable that the peculiar smells of animal fats, of sweat, and of the animals, which are so distinct, that it is quite easy to discriminate by the smell the origin of different fats, are owing to these acids. Human sweat has a distinct odour of caprylic acid. Redtenbacher has found traces of these volatile acids in all animal fats, along with oleic acid, or rather oleine.

ACTION OF ALKALIES AT A HIGH TEMPERATURE ON OLEIC AND ELAIDIC ACIDS.

When these acids are heated with three volumes of strong alkaline ley till the water is dissipated, and the alkali begins to melt, a violent effervescence occurs, owing to the escape of free hydrogen gas. Water is here evidently decomposed, its oxygen uniting with some of the elements of the oily acids. The alkali is found to be united with a

new acid and with acetic acid. If the mass be acted on with a little water, the salt of the new acid separates as a soap.

The oily acid of this soap is separated and purified in the usual way. It crystallizes from alcohol, melts at 143° , and is friable. Oleic and elaidic acids yield the same new acid. According to Varrentrapp, its discoverer, its formula is $C_{32}H_{30}O_3, HO$. This explains its formation: for if from

$$\begin{array}{rcl} 1 \text{ at. Oleic Acid} & . & C_{36}H_{34}O_4 \text{ we subtract} \\ 1 \text{ at. of the new Acid} & . & C_{32}H_{30}O_3 \\ \hline \text{there remain} & . & C_4H_4O_3. \end{array}$$

Now $C_4H_4O_3 + O = C_4H_4O_4$, that is, 1 at. acetic acid. The 1 at. of oxygen is obtained from water, and 1 at. of hydrogen is disengaged. The same explanation, of course, applies to elaidic acid.

OLEIC ACID OF THE DRYING OILS.

Linoleic Acid.—Sacc has lately investigated linseed oil, the most important of the drying oils, and has found it to contain some margarine and a large proportion of an oleine, the acid of which differs from oleic acid. According to his analysis this acid is $C_{46}H_{38}O_5, HO$. But, as it is even more readily altered by the oxygen of the air than ordinary oleic acid, this analysis cannot be considered as decisive.

This acid, which may be called *Linoleic acid*, resembles melted oleic acid in its physical properties, but differs from it in not crystallizing, and in its tendency to dry up into a varnish by absorbing oxygen from the air, a property which it communicates to its compound with oxide of glycercyle, a compound which forms the chief constituent of the drying oils.

When acted on by nitric acid, linoleic acid is converted into a resinous mass, which by further oxidation yields a large proportion of suberic acid, also pimelic, oxalic, and carbonic acids and water. It would appear, however, that the pimelic acid is only formed when the linoleic acid contains margaric acid, in which case succinic acid also appears among the products.

ACIDS OF CASTOR OIL.

When castor oil is saponified, the soap yields a mixture of two oily acids: one solid at ordinary temperatures, the other liquid.

The former melts at 266° , forms soaps with alkalis, and has been called Margaritic Acid. Formula, $C_{35}H_{31}O_6?$. (Bussy and Lecanu, Laurent.)

The latter congeals at 21° . Its properties and composition may be considered unknown. It is called ricinic acid.

Castor Oil.—This oil is a mixture of the compounds of oxide of glyceryle with the acids last mentioned. One of these oils is a fusible margarine or fat, the other liquid. Both differ from ordinary margarine and oleine.

Castor oil is extracted from the seeds of *Ricinus communis*. It is, when pure, pale, viscid, and nearly devoid of taste or smell. Its use as a purgative is well known. It is completely soluble in its volume of absolute alcohol, which furnishes the means of detecting its adulteration with other oils. By nitrous acid it is slowly converted into palmine, a substance analogous to elaidine, but differing from it, and most probably derived from the ricinine, the compound of ricinic acid with glycerine, as elaidine is from oleine. Palmine, when saponified, yields a new fatty acid, palmic acid, $C_{34}H_{32}O_5.HO$. (Playfair.)

Cenanthylic Acid.—When castor oil is heated with nitric acid, it yields a volatile acid of an agreeable aromatic odour, which has been called cenanthylic acid. It belongs to the series $(CH)_n + O_4$, and has already been mentioned as a product of the oxidation of oleic acid by nitric acid. It is probably derived from oleic acid, which may be present in the castor oil, or from ricinic acid which is analogous to oleic acid, possibly essentially the same.

APPENDIX TO THE OILY ACIDS.

NATURAL FIXED OILS AND FAT.

The term fixed oil, or fat, in general signifies a compound of oxide of glyceryle with certain organic acids. Such compounds are exclusively natural products, not one having as yet been formed artificially.

Among animals they occur chiefly in the cellular membrane; among plants in the seeds, capsules, or pulp surrounding the seed; very seldom in the root. They all, when fluid or melted, make a greasy stain on paper, which is permanent. They are decomposed by acids, which combine with or destroy the oxide of glyceryle; and by alkalis, which unite with the acids, setting free the oxide of glyceryle. The latter process is called saponification, because the compounds of the oily acids with alkalis have the properties of soap.

The most abundant oils and fats are compounds of oxide of glyceryle with stearic, margaric, and oleic acids; two of these, and often all three, being present. Indeed, neither stearate, margarate, nor oleate of oxide of glyceryle is yet known in a state of purity. From what has been said of these three compounds, which for brevity we shall call stearine, margarine, and oleine, the consistence of the oil or fat de-

pend on the predominance of one or other. Where stearine predominates, the fat is firm and solid; if margarine be most abundant, it is soft, like lard; while, if oleine predominate, it is liquid. It is obvious that a mixture of stearine and oleine in certain proportions will have the consistence of margarine.

Fixed oils and fats are generally inodorous. Where they possess a peculiar smell, this is always owing to the presence of a compound of oxide of glyceryle with a volatile oily acid, such as butyric or capric acid.

Fats are more fusible than the acids they contain; but at low temperatures they are harder. By pressure between warm plates, the greater part of the oleine of fats may be separated. The remaining fat is harder, less fusible, and less greasy, in proportion as it approaches to pure stearine. At low temperatures the oils assume exactly the aspect of fats. The solid parts of fats and oils are sometimes nearly pure stearine or margarine; in other cases they are definite compounds of stearine or margarine with oleine. Such is the case with the solid part of olive oil, and with the butter of *Theobroma cacao*.

Oils and fats may be divided into two well-marked classes, according to the action of atmospherical air, or of nitrous acid and nitrate of mercury, on them.

The first of these classes contains the drying oils; so called, because when exposed to the air, they absorb oxygen, and are converted into a transparent, tough, dry mass, or varnish. The drying oils, moreover, are not solidified by nitrous acid or nitrate of mercury.

Sacc has recently shewn that linseed oil, the most important of the drying oils, consists of 1 eq. margarine (margarate of oxide of lipyle) and 10 eq. linoleine (linoleate of oxide of lipyle). As a drying oil, its properties are much obscured by the presence of mucilage, derived from the seeds; but when this is removed, as recommended by Liebig, by agitating the oil with litharge and diluted sulphuric acid, or by rubbing it up with sulphate of lead, the mucilage is carried down by the powder, when allowed to deposit, and the clear oil then rapidly dries up into a varnish, which has very little colour.

Linseed oil is very easily saponified, either by alkalies or by digestion in a moderate heat with oxide of lead (litharge). The latter process is perhaps the most advantageous method of preparing glycerine, the proportion of which in linseed oil is larger than in other oils.

The second class, which may be called that of the fat oils, contains those oils and fats which do not dry on exposure to the air, and which, when liquid at ordinary temperatures, are solidified by nitrous acid or nitrate of mercury.

Owing to the impurities which oils and fats in their natural state contain; such as membrane, mucus, or albumen, and which act like yeast in promoting chemical action, most of them, when kept, become rancid, as it is called. This change is produced by the absorption of oxygen in part, while the oily acids are set free, and sometimes, as in palm oil, oxide of glyceryle is liberated. The rancid smell is owing to the production, at the expense of the elements of the oxide of glyceryle, the impurities, and the oxygen of the air, of a volatile body which appears to be acid, as alkalis remove it. Pure stearine, margarine, and oleine do not become rancid.

ACTION OF HEAT ON OILS AND FATS.

The action of heat on oils is very remarkable. At a high temperature they boil, giving off carbonic acid with a little inflammable gas, and a substance, *Acroleine*, possessed of a most pungent odour, attacking the eyes most painfully. They acquire a darker colour, and, on cooling, generally assume the consistence of butter or lard. Oils when distilled become more solid, fats less solid.

When the drying oils are heated, they become thick and viscid, and afterwards dry much more rapidly than before. Hence the advantage of boiling oils intended for oil varnish.

When the fixed oils and fats are distilled, they yield, besides carbonic acid and inflammable gas, a crystalline product, principally margarinic acid, mixed with sebacic acid, arising from the oleic acid, acroleine, proceeding from the oxide of glyceryle, and an oily liquid, insoluble in alkalis, which is commonly a carbohydrogen. A portion of oleic acid also distils unchanged. The first half of the product is solid, owing to the predominance of margarinic acid; the second half liquid. No stearic acid is found in either; it is converted into margarinic acid.

It has already been stated that the sebacic acid arises exclusively from oleic acid, whether from fat or drying oils, with the exception of castor oil, which does not yield it. Stearinic and margarinic acids, as well as pure stearine and margarine, do not yield a trace of it.

On the other hand, none of the known oily or fat acids, when distilled alone, yields the smallest trace of acroleine, the substance to which is owing the insupportably pungent smell of distilled oils or fats. We can only, therefore, ascribe the origin of acroleine to the action of heat on oxide of glyceryle; and, in point of fact, hydrated oxide of glyceryle (glycerine), when distilled alone, yields it in large proportion. Hence the occurrence of acroleine among the products of the distilla-

tion of a fat or oil is a sure and delicate test of the presence of glycerine in the oil. Acroleine has been already described under Glyceryle as the hydrated oxide of acryle.

Castor oil, so peculiar in other respects, yields also peculiar products when heated. Among the products are acroleine, an oil insoluble in alkalies, and some peculiar fatty acids. When about one-fifth of the oil has been decomposed, the residue in the retort suddenly consolidates into a spongy elastic yellow mass, insoluble in all menstrua except strong alkalies, with which it forms a viscid solution.

The oil, insoluble in alkalies, contains a solid and a liquid compound. The fatty acids obtained are two: one solid and volatile, the other liquid; both as yet little examined. No sebacic acid occurs in this process.

When castor oil is distilled with nitric acid, a volatile acid is produced, possessing the formula $C_{14}H_{13}O_3 + aq.$ This formula differs from that of the œnanthic acid by 1 at. oxygen, and it has hence been named œnanthylic acid.

OIL GAS.

When fixed oils are introduced drop by drop into red-hot vessels, they are almost entirely converted into volatile products. Of these a large portion consist of permanent gases,—carbonic oxide, marsh gas, and olefant gas,—mixed with the vapours of several very volatile liquids. This mixture is oil gas. Owing to the presence of olefant gas and of the vapours above mentioned, its illuminating power is twice that of the best coal gas, and three and a half times that of ordinary coal gas. But this difference is barely sufficient to cover the increased expense of the oil employed, even when of the coarsest quality. The sp. gr. of the best oil gas is 0.900.

When oil gas is strongly compressed, as in the process for rendering it portable, the vapours above mentioned are liquefied. Faraday, who examined the liquid, discovered in it several compounds of carbon and hydrogen. One of these is pure benzole. (See Benzole.) Another is liquid at 0° or -1° , but gaseous at 32° . It has the same composition in 100 parts as olefant gas, but twice the density. Hence its formula is double that of olefant gas. It has been named quadro-carburetted hydrogen. The mixed liquid appears to contain another volatile substance, which, like the benzole, crystallizes at low temperatures, the exact composition of which is not sufficiently known; and in the less volatile portion, another liquid, having apparently the composition, in 100 parts, of olefant gas. The great illuminating power of oil gas is owing to the presence of the vapours of these carbohydro-

gens. For details the reader is referred to the *Memoirs of Faraday* in the "*Philosophical Transactions*."

ACTION OF SIMPLE SUBSTANCES ON FIXED OILS.

The action of oxygen has been already mentioned. The fixed oils are decomposed by chlorine and bromine, yielding hydrochloric and hydrobromic acids, along with other products not yet examined. They generally dissolve iodine, forming a brown solution. They also dissolve sulphur and phosphorus, and such solutions are occasionally used in medicine. When strongly heated with sulphur, the oils undergo a change not yet investigated. The mixture thus formed is called balsam of sulphur. For use it is dissolved in oil of turpentine or oil of aniseed.

ACTION OF ACIDS ON FIXED OILS AND FATS.

1. ACTION OF SULPHURIC ACID.

The oils are decomposed by strong sulphuric acid. If the quantity of acid be small, it combines with the oxide of glyceryle, setting free the oily acids. But when more acid is used, very remarkable changes occur, which have been studied by Fremy in the case of olive oil.

When sulphuric acid is gradually added in the cold to twice its volume of olive oil, bisulphate of the oxide of glyceryle is formed on the one hand, and on the other compounds of sulphuric acid with margaric and oleic acid. The mixture becomes tough; and if mixed after twenty-four hours with two volumes of water, the sulphates of the oily acids, being insoluble in the diluted acid, rise to the surface as a syrupy liquid. This mixture, when freed from adhering acid by washing with a little cold water, dissolves in a larger quantity of water. The sulphate of margaric acid has not yet been separated from that of oleic acid; but the solution containing these compounds is decomposed when kept, or when heated, yielding five new acids. (Fremy.)

When the solution is long kept at ordinary temperatures, the sulphuric acid separates; a mixture of two new acids, metamargaric and metoleic acids, rises to the surface; and a third, hydromargaric acid, remains dissolved in the water along with the sulphuric acid. If the original solution be heated, there rises to the surface a mixture of these three acids, with a fourth, hydroleic acid; and, when this mixture is boiled with alcohol, there is deposited on cooling a fifth acid, hydro-

margaric acid, which appears to be formed by the mutual action of metamargaric and hydromargaritic acids. (Fremy.)

Metamargaric Acid.—Symbol, $\overline{mMr}, 3HO?$ The mixture deposited in the cold by the above solution is exposed to strong pressure to separate the metoleic acid, and the residue purified by crystallization from alcohol, in which the latter acid is sparingly soluble. Metamargaric acid is a white solid, fusible about 112° , and crystallizing on cooling. It is insoluble in water, soluble in alcohol and ether.

When heated with oxide of lead, it loses 3 at. of water, which appear to be replaced by 2 at. of oxide,—a very unusual occurrence, if confirmed. Its salts have been little studied; but it seems to form with potash, soda, and ammonia, neutral and acid salts, the former gelatinous, the latter soluble in alcohol, and crystallizable.

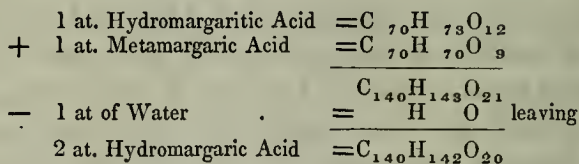
Hydromargaritic Acid.—Symbol, $\overline{hMt}, 2aq.?$ When the solution above mentioned has ceased to deposit any more metamargaric and metoleic acids, it is boiled, when a mixture of hydromargaritic and hydroleic acids rises to the surface. Cold alcohol removes the latter, and leaves hydromargaritic acid as a white solid, insoluble in water, but soluble in alcohol and ether. It forms colourless prisms, which are friable, and melt at 155° . By heat it is resolved into water and metamargaric acid. Its salts resemble those of the preceding acid, but are as yet little known.

Hydromargaric Acid.—Symbol, $\overline{hMr}, 2HO?$ This acid, as already stated, is formed when the mixture containing the two preceding acids, along with the two remaining ones, is boiled in alcohol. On cooling, the new acid is deposited in crystals. It is best obtained by melting together 1 eq. of the two preceding acids, and crystallizing the mass from alcohol. It generally crystallizes in large hemispherical masses, is much more soluble than the two acids from which it is formed, and melts at 140° . It forms a series of salts, which, although analogous, are quite distinct from those of the preceding acids. By the action of heat it yields metamargaric acid.

ON THE COMPOSITION OF THE THREE PRECEDING ACIDS.

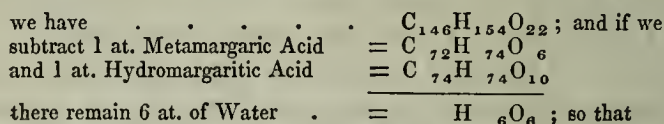
Fremy, the discoverer of these acids, has proposed a very simple explanation of their formation. Adopting for hydrated margaric acid the formula $C_{70}H_{69}O_8$, he considers hydromargaric acid to be formed from it by the assimilation of the elements of 4 at. water; and its formula will be $C_{70}H_{73}O_{12} = C_{70}H_{71}O_{10}, 2HO$; while metamargaric acid is formed from margaric acid by the addition of 1 eq. of water, the

formula of the hydrated metamargaric acid being $C_{70}H_{70}O_9 = C_{70}H_{67}O_6, 3HO$. But not only is the formula thus adopted for margaric acid irreconcilable with the analyses of Varrentrapp, but the analyses of the new acids by Fremy do not sufficiently support his formulæ. Fremy adopts for hydromargaric acid the formula $C_{70}H_{71}O_{10}$, and considers it as formed from



But if the preceding formula be erroneous, this cannot be a correct account of its production.

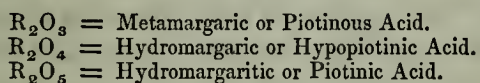
If we consider hydromargaritic acid a bibasic acid, and deduce its composition from its analysis as contained in the salt of silver, we obtain the formula $C_{74}H_{74}O_{10}$; and for the hydrate, $C_{74}H_{76}O_{12}$. If now we subtract 2 at. of carbonic acid and 2 at. of water, there remain $C_{72}H_{74}O_6$; proportions which agree much more closely with the numerical results of Fremy's analysis of the anhydrous metamargaric acid than the formula which he has adopted, namely, $C_{70}H_{67}O_6$; and which, moreover, explain the conversion of hydromargaritic acid into metamargaric acid by the action of heat. With regard to hydromargaric acid, the analysis of Fremy may be better interpreted by the formulæ $C_{73}H_{75}O_9$ for the dry, and $C_{73}H_{77}O_{11}$ for the hydrated acid, than by those he has chosen. If we take the formula of the hydrated acid on this supposition, and double it,



the production of this acid from the other two may be as easily explained as on Fremy's view. Hitherto, however, the atomic weights of these acids, as deduced from their salts, agree with neither of the above views. Indeed, although, according to the views of Fremy, all these acids differ only in the proportion of the elements of water they contain, so that hydrated metamargaric acid contains only 1 eq. of water more than margaric acid, while the acids in their salts would be isomeric; and, moreover, anhydrous hydromargaritic acid has the same formula as hydrated hydromargaric acid, and anhydrous hydromargaric acid the same formula as hydrated margaric acid; yet we cannot adopt these views, since we know that margaric acid is not $C_{70}H_{69}O_8$, but $C_{68}H_{68}O_8$.

The more recent researches of Varrentrapp and Miller have thrown some doubt on the exactness of the numerical results of Fremy, on which both the above views are founded. According to Miller, both hydromargaric and hydromargaritic acids become solid about 35° below the point at which they melt; a fact which excites the suspicion that they may both be mixtures of two distinct compounds.

Berzelius has proposed a third view of the composition of these acids, also founded on the analysis of Fremy. He assumes the existence of a radical, *piotine* = $C_{35}H_{35}$. Calling this = R_2 , we have



The resulting formulæ, when calculated to 100 parts, agree most exactly with the actual numerical results of Fremy; but not only are these doubtful, but, by adopting the formulæ of Berzelius, we lose all insight into the formation of these acids from margaric acid; and this is the chief object of the analytical investigation.

To shew how little confidence is due to the coincidence of numbers when unsupported by the study of the nature of the substance, and the products accompanying its formation, it may be stated, that, if we choose to consider hydromargaritic acid as the acid margarate of ethyle, which it certainly is not, the formula $\overline{Mr}, AeO, 3HO = C_{74}H_{75}O_{12}$, when reduced to 100 parts, gives numbers exactly corresponding to Fremy's analysis of the acid.

METOLEIC AND HYDROLEIC ACIDS.

These acids arise from the action of sulphuric acid on oleic acid, as the three former do from margaric acid.

Metoleic Acid.—Symbol, $\overline{mOl}, 2HO$. When metamargaric acid is prepared as before described, this acid remains undissolved by the alcohol. It is purified by repeated boiling with alcohol and exposure to cold, when the metamargaric acid crystallizes out. It is a liquid, insoluble in water, very soluble in ether, and by heat converted into carbonic acid and a carbohydrogen. It is distinguished from oleic and hydroleic acid by its sparing solubility in alcohol. According to Fremy, in its salts 1 at. of water is replaced by 2 at. of base, which is very unlikely.

Hydroleic Acid.—Symbol, $\overline{hOl}, 2HO$. In the preparation of hydromargaritic acid, hydroleic acid is removed by cold alcohol, in which it is extremely soluble, and by which it may be purified. It forms a

liquid, insoluble in water, very soluble in alcohol and ether. Heated with oxide of lead, it loses 2 at. of water, which are replaced by 2 at. of oxide. In its other salts, according to Fremy, 2 at. of base only displace 1 at. of water.

When these acids are distilled, they yield carbonic acid; two liquid carbo-hydrogens, oleène and elaène, both having the composition of olefiant gas; and an empyreumatic oil. (Fremy.)

The two carbohydrogens are separated by careful rectification. Oleène, the more volatile, boils at 131° , has an alliaceous smell, is very combustible, and appears to have poisonous properties. Elaène boils at 230° , has a smell like that of oleéne, and is decomposed by chlorine, with the production of hydrochloric acid and a new liquid compound.

Fremy adopts for metoleic acid the formula $C_{70}H_{63}O_8, HO$; but the analysis of the salt of silver rather indicates that it is a bibasic acid, and that its formula is $C_{90}H_{85}O_{10}, 2HO$. This formula readily explains the action of heat; for if from 1 at. of the hydrated acid $= C_{90}H_{87}O_{12}$ we subtract 5 at. of carbonic acid and 2 at. of water $= C_5H_2O_{12}$

there will remain $C_{85}H_{85}$.

This may be divided into $C_{40}H_{40} = \text{oleène}$, and $C_{45}H_{45} = \text{elaène}$. The calculated density of elaène in the state of vapour agrees with Fremy's experiment. The compound formed by chlorine seems to be $C_{45}H_{40}Cl_5$, in which 5 at. of hydrogen are replaced by 5 of chlorine.

According to Fremy, hydroleic acid only differs from metoleic acid in containing the elements of 1 at. of water more. This admits of the same explanation of the action of heat, which is the same in both acids. It is obvious that the whole of these new acids must be examined anew.

2. ACTION OF NITROUS ACID ON OILS.

It has been already stated, under the head of Oleic and Elaidic Acids, that oleic acid is solidified by nitrate of mercury or nitrous acid. Pou-tet first observed this action in the case of olive oil and several other oils. Boudet shewed that nitrous acid is the true agent, and that oleine (oleate of oxide of glycyle) is converted by it into elaidine, a solid fat, which is composed of elaidic acid and oxide of glycyle.

When olive oil, for example, is mixed with the common red fuming nitric acid of commerce, it is solidified by the nitrous acid present. According to the quantity of nitrous acid, the change is effected in a longer or shorter time. When a mixture of 3 parts pure nitric acid

and 1 part hyponitrous acid (produced by the distillation of nitrate of lead) was used, the following results were obtained:—

1 part of the Acid mixture with 33 of Olive Oil solidified in 70 minutes.		
1	50	78
1	75	84
1	100	180
1	200	435
1	400	remained unchanged.

The very small quantity required to produce the effect, and the fact that in several oils, castor oil, for example, a similar solidification is caused by sulphurous acid, render this action a problem which is yet unresolved. According to Gottlieb, the formation of elaidine is due to the conversion of oleic acid into the isomeric elaidic acid; but the mode of action of the nitrous acid remains as obscure as ever.

Oil of almonds, of acacia nuts, of rape seed, castor oil, and oil of hazel nuts, agree with olive oil in being solidified by nitrous acid or nitrate of mercury. The oils of linseed, hemp, walnuts, poppy seed, and other drying oils, undergo no change when mixed with these reagents, except that they are coloured brown. The presence of drying oils prevents or retards the solidification of the fat oils.

The product of the action of nitrous acid on the fat oils is the same in all cases, except in that of castor oil. A yellowish semi-solid mass is formed, which, when washed with alcohol, becomes white, and when further purified by pressure and crystallization is pure elaidine. The yellow matter taken up by the alcohol changes to a dark brick-red by the action of alkalis.

Those oils which yield elaidine generally contain margarine and oleine; but the former in these circumstances yields no part of the elaidine; for pure margaric acid cannot, like oleic acid, be converted into elaidic acid. The elaidine from almond oil appears to contain unchanged oleine, and that from olive oil margarine. If this be really the case, the purest elaidine yet obtained cannot be considered as pure elaidate of oxide of glyceryle. Pelouze and Boudet stated, that, when margaric acid is dissolved in oleic acid, both are entirely converted into elaidic acid. But Gottlieb has shewn that this is not the case.

The oleine of human fat and of hog's lard, as well as that of the oils above mentioned, is converted by nitrous acid into elaidine. But neither the solid part of these and other fats, pure stearine, nor pure stearic acid, can be made to undergo this change.

Elaidine made from olive oil melts at about 90°. When saponified, the soap, treated with acids, yields elaidic acid, which is probably impure, as it melts at 107° and lower, while pure elaidic acid, made from

pure oleic acid melts at about 112° , and is isomeric with oleic acid. (Gottlieb.)

Palmine.—Castor oil, when treated with nitrous acid, yields a peculiar new fat, palmine, which melts at 143° . When saponified by alkalies, it yields oxide of glyceryle, and a new fatty acid, palmic acid.

Palmic Acid.—The soap made from palmine and potash being purified, is decomposed by tartaric acid, and the fatty acid which separates is dissolved in cold alcohol. The solution, by spontaneous evaporation, yields pure hydrated palmic acid. It is crystallizable, and melts at 122° ; it is very soluble in alcohol and ether. When boiled with alcohol, it seems to form palmate of oxide of ethyle; at least, an oily liquid separates on cooling. It is partially decomposed by distillation. Its salts are little known; and the composition both of palmine and palmic acid is yet undetermined.

It is very remarkable that a current of sulphurous acid gas, when passed through castor oil, converts it into a solid mass, which seems to be palmine, and which, when saponified, yields palmic acid. That the same acid should be formed by an oxidizing and a deoxidizing agent, is a fact which requires a careful investigation.

ACTION OF METALLIC OXIDES ON FIXED OILS AND FATS.

The action of alkalies and of oxide of lead on fixed oils and fats has long been practically known. The compounds produced by the former are called *Soaps*: those formed by oxide of lead are *Plasters*.

Up to 1813 soaps and plasters were considered to be compounds of alkalies and oxide of lead with oils and fats; although it was observed that the oil, when again set free, had acquired a greater solubility in alcohol, and was more readily saponifiable than before. The discovery of glycerine by Scheele was the only well ascertained fact previous to the researches of Chevreul in 1813.

This illustrious philosopher observed that a certain kind of soap, when diluted with a large proportion of water, became turbid, and deposited a pearly substance, which he found to contain an alkali combined with an oily matter, not previously described, of decided acid properties. This observation was the origin of, perhaps, the most splendid series of investigations known in the history of chemistry; in the course of which, continued as they were for fourteen years, Chevreul not only discovered a large number of new compounds, and cleared up the whole subject of the fixed oils, fats, soaps, and plasters, but established those principles which at present prevail in the study and analysis of organic substances.

At a time when such investigations were unknown in organic chemistry, the profound sagacity of this distinguished philosopher taught him that the ultimate analysis of an organic compound was not alone sufficient to determine its true composition, but must be accompanied by a complete study of the changes produced on it by the action of reagents, and a careful determination of the quantities of the several products as well as of their composition.

This great principle, which now regulates all researches in organic chemistry, we owe to Chevreul. By it he was led to numerous discoveries, and by it also he was guarded from error, at a time when all was error in this branch of chemistry. But the example of Chevreul was not immediately followed; and it was not till Dumas and Boullay, in 1824, applied the same principle to the study of the ethers, that its application to organic chemistry in general gave rise to the extraordinary progress which, since that time, has been made in this department of the science.

Chevreul shewed that the different kinds of fixed oils and fats contained three distinct compounds, united in the most various proportions: one, liquid at ordinary temperatures, which he called Oleine; and two solid, but differing in fusibility, Stearine and Margarine.

He also shewed that each of these contained oxide of glyceryle (glycerine) in combination with an oily acid; and that when the oil or fat was acted on by alkalies, or by oxide of lead or zinc, these bases united with the oily acids; forming, in the first case, soluble soaps; in the other, insoluble plasters. The oxide of glyceryle, in the moment of separation, united with water, forming hydrated oxide of glyceryle (glycerine, or sugar of oils). When the weight of the glycerine was added to that of the oily acids, after the latter were separated from the bases, their united weights exceeded somewhat that of the original oil; which he shewed to arise from the fact, that both the oily acids and the glyccrine, when separated from other substances, combine with water. With ordinary oils and fats no other products are formed; but when the oil or fat contains any of the volatile oily acids, such as butyric or phocenic acids, the soap contains a salt of the volatile acid, and acquires its smell.

Soaps are divided into *hard* and *soft soaps*. The former are obtained from fats or fat oils, the latter from drying oils. Of the hard soaps, those containing soda are firmer than the soaps of potash. Of the hard soaps of commerce, those made with vegetable oils are mixtures of oleate and margarate of potash or soda; those made with animal fats are mixtures of stearate, margarate, and olcate of potash or soda.

In order to form soap, the oil or fat is boiled with a solution of caustic potash or soda, till the whole forms a thick viscid emulsion, which can be drawn out into long clear threads. If not clear, either water or alkali must be added, according as the turbidity depends on undecomposed oil, or on a deficiency of water. When the saponification is complete, the next step is to separate the soap from the excess of alkali, the glycerine, and the superfluous water. This may be effected by boiling down till the alkaline ley becomes very concentrated, when the soap becomes insoluble, and rises to the surface. The same end is attained by adding very strong ley, or common salt, both of which render the soap insoluble when added in sufficient quantity; soap being absolutely insoluble in alkaline ley of a certain strength, as well as in a saturated solution of common salt. The separation is known to be complete when the liquid ceases to froth in boiling; and the soap is ladled off into moulds, where it is well stirred to favour the separation of the liquid, which should run off from its surface like water from fat. The soap brought to this state in the first operation is called *grain soap*, from its separating in grainy particles at first. It may be further purified by repeating the process of dissolving it in alkaline ley, and separating it by the addition of salt. In this process the impurities subside, and the soap generally takes up more water; so that, although whiter, it is less strong. White soap, for example, commonly contains 45 to 60 p. c. of water, while grain soap only contains 25 to 30 p. c. No doubt it might be again procured with as little water as at first; but it is the fluidity caused by the additional water that allows the impurities to subside, and the soap to become white. What is called marbled soap is grain soap which has not been subjected to purification; and the grey, blue, and green colours in it arise principally from the presence of insoluble soaps of oxide of iron or of copper.

It is to be observed, that when common salt is added to the solution of a soap of potash, the latter is converted into soda soap, entirely or partially, according to the quantity of salt, while chloride of potassium is formed. As this latter salt does not cause the soap to separate, like common salt, it is necessary to use twice as much salt to separate the soap when it has been made with potash. If a soap of potash be required, it must be separated by caustic potash. In Germany soda soap is first made with potash, and the potash soap is decomposed by common salt. In England and France, soda soap is made directly with caustic soda.

The use of salt in this important process depends on the curious fact, that soap, like muscular fibre or animal membrane, cannot be

moistened by a saturated solution of salt; that is, cannot deprive it of water. On the other hand, if these substances be moistened with water, or dissolved in it, the addition of dry salt in sufficient quantity will remove the whole of the water.

Soft soaps are made with drying oils, either alone, or mixed with train oil or other fat oils. They are insoluble in strong alkaline ley, and are separated from water by the addition of potash or soda. When train oil is added, they have the disagreeable smell of that oil, arising from phocenic acid.

Such is a very general and brief account of the principles of soap-making, which are few and simple. The great experience of the makers of a substance so long known had taught them empirically how to produce good soap in a great variety of forms; but it is only of late that the rationale of their processes has been understood, and that improvements have been made on scientific principles. Soap-making may now be considered as one of the arts most thoroughly understood.

It is impossible here to describe the varieties of soap. Of the simple soaps, stearate of soda may be considered as the type of hard soaps. It is hardly altered by contact with 10 parts of water. Stearate of potash, with 10 parts of water, forms a viscid solution. The margarates of soda and potash resemble the stearates. Oleate of soda dissolves in 10 parts, oleate of potash in 4 parts of water. Hence soaps are harder and less soluble the more stearate and margarate they contain; and softer and more soluble when oleates predominate.

As the soaps of lime, baryta, earths, and metallic oxides in general, are insoluble, the use of hard water, which contains salts of lime, causes a precipitation of the insoluble soap, which is very prejudicial. This may be corrected by adding to the water as much carbonate of soda or potash as is sufficient to separate all the lime, before the water is used to dissolve soap. It is in this way that soda renders hard water soft for washing and other purposes.

The soap used in medicine is a hard soap made by boiling to dryness in a gentle heat 1 part of soda ley, sp. gr. 1.33, and 2 parts of olive or almond oil. It is a mixture of margarate and oleate of soda with free soda and glycerine. *Antimoniated soap* is made by dissolving 1 part of precipitated sulphuret of antimony in caustic potash, mixing the solution with 6 parts of medicinal soap, and evaporating to dryness.

PLASTERS.

There are two kinds of officinal plaster made with lead,—litharge plaster, and white lead plaster; but all the compounds of oxide of lead with the oily acids possess the properties of plaster.

Litharge Plaster, or Diachylon plaster, is made by boiling 5 parts of levigated litharge (protoxide of lead) with 9 of olive oil, and some water, till the whole acquires a proper consistence and a greyish white colour. At common temperatures it is plastic; when heated, it melts. It may also be obtained by adding subacetate of lead to a solution of soap. The plaster thus formed is good at first, but afterwards becomes hard; while that prepared directly from the oil remains plastic, apparently from the presence of undecomposed oil. Litharge plaster consists chiefly of basic oleate and margarate of lead. It is the basis of almost all medicinal plasters.

White-lead plaster (*Emplastrum cerussæ*) is made in the same way, using 16 parts of carbonate of lead to 9 of olive oil. It is white, plastic in the heat of the hand, liquid at 212° . It enters into the composition of many plasters used in medicine.

Iron plaster and *Mercurial plaster* are made by adding salts of mercury or iron to solution of soap. They are insoluble masses, softened by heat, and are not much used.

OILS AND FATS OCCURRING IN NATURE.

1. DRYING OILS.

The drying oils are generally derived from seeds by pressure. Their distinguishing character is that of drying into a varnish by exposure to the air. This change is caused by the absorption of oxygen; and, as the impurities generally present in oils impede the access of oxygen to the particles of the oil, the drying takes place much more rapidly when these impurities are removed or destroyed. Boiling acts by destroying them, and a little litharge is added to promote the change. But a better and more colourless varnish is obtained by agitating the drying oil, linseed oil for example, with a mixture of water, litharge, and subacetate of lead, without heat. When the whole is allowed to stand the impurities subside with the water, and the oil is so pure, that it dries into a varnish in twenty-four hours. It contains a little oxide of lead, but this rather improves the varnish.

The absorption of oxygen by drying oils goes on so rapidly when

their surface is much extended, that wool, shavings, tow, or other porous substances, when steeped in drying oil, and exposed to the air, often take fire spontaneously, from the heat developed. This is a frequent cause of fire in manufactories, where the oiled parts of machinery are wiped with tow or cotton.

The oil or varnish for printer's ink is made by boiling drying oil till it acquires the proper consistence, and the tendency to dry quickly.

The following are the principal drying oils:—*Linseed oil*, from the seeds of *Linum usitatissimum*. It has the properties of drying oil in the highest degree. *Walnut oil*, from the kernel of the walnut, *Juglans regia*. This oil stands next to the preceding as a drying oil, *Hempseed oil*, from the seeds of *Cannabis sativa*. *Oil of Poppy-seed*. *Croton oil*, from the seeds of *Croton tiglium*. The oils of *Jatropha multifida* and *Jatropha curcas*, resembling croton oil in activity and other properties. The oils of *Euphorbium lathyris* and of *Curcubita pepo* are also drying oils.

2. FISH OR TRAIN OILS.

Under the name of train oil several varieties of fish oil are known. They have some resemblance to the drying oils; but are distinguished by containing in general one or more volatile oily acids in small quantity, generally phocenic acid. They are for the most part composed of oleine with a little phocanine, which is probably valerianate of oxide of glyceryle, and, if so, should be called valerine. The principal varieties are *whale oil*, *seal oil*, *dog-fish oil*, and *cod's liver oil*. Most fish oils contain a small quantity of a crystallizable fatty acid, not yet examined. That of the dolphin holds a portion of spermaceti dissolved. Fish oil is used for lamps, and to mix with drying oils for soft soap.

3. LIQUID FAT OILS.

These are distinguished from the drying oils by the action of the air; if exposed to it, they are slowly altered, but remain greasy, and do not yield a dry varnish. They are used both as food and for burning. They are purified from foreign matters by being agitated with a little oil of vitriol, and afterwards washed with water to remove any adhering acid. After this operation they burn much more brightly, and elog the wick much less. They are all more or less completely solidified by nitrous acid, which is not the case with drying oils.

The principal fat oils are *olive oil*, from the pulp of the olive, *Olea*

europæa, which is much used as an article of food and for making soap. It congeals when exposed to cold, and the solid portion seems to be a compound of margarine and oleine. *Almond oil* contains much less margarine than olive oil. It therefore yields softer soap, and is better adapted to the preparation of oleic acid. *Rapeseed oil* and *oil of Colza* are similar to olive oil, and much used as combustibles on the Continent.

The *oil of yolk of egg* and *oil of cow-heel* are two mild inodorous animal oils, very similar to vegetable oils. The former soon becomes rancid; but the latter, from retaining its sweetness very long, is much prized for fine salves and ointments.

4. SOLID FAT OILS, OR FATS.

These are numerous, both in the vegetable and animal kingdoms, and are known by various names, such as tallow, suet, lard, butter, and fat.

Laurel fat is obtained from laurel berries by boiling and pressure. It is soft and green, and is used for salves. It is chiefly composed of laurine, or laurate of oxide of glyceryle, (oxide of lipyle,) along with a green liquid fat, probably oleine.

Butter of Cacao, from the beans of *Theobroma cacao*, is white, solid, and rather brittle. It does not become rancid; the greater part of it is a crystalline compound of oleine and stearine, melting at 85°.

Butter of Nutmegs, from the nuts of *Myristica moschata*, is solid, yellow, and possessed of the aromatic smell of the essential oil of nutmegs. Cold alcohol dissolves a fat oil, the essential oil, and the colouring matter, leaving 25 to 30 p. c. of a white crystalline fat, fusible at 87°. This fat resists the action of diluted alkalies, but is quickly saponified by fusion with hydrate of potash. The soap thus formed yields a crystallizable acid, fusible at 122°. This is myristic acid; and the fat is myristate of oxide of glyceryle, or sericine. (Playfair.)

Butter of Cocoa-nuts, from the fruit of *Cocos nucifera*, is white and soft, fusible at 68°, and consists of two oils, one liquid, the other solid, at ordinary temperatures. The latter is cocinate of oxide of lipyle; the former, probably oleine. This butter soon becomes rancid.

Palm oil or *butter*, from the rind of the fruit of *Avoira elais*, *Elais Guianensis*, is yellow and semi-solid, with a smell of violets. When new, it melts at 81°; when long kept, at 90° to 96°. It easily becomes rancid, glycerine being set free, and at the same time the fatty

acids. It contains oleine, margarine?, and about two-thirds of its weight of a white solid fat, which is palmitine, and which contains palmitic acid. (Fremy, Stenhouse.) Palm oil is much used for making soap. If white soap is desired, the oil must be bleached; which may be done either by exposure to the sun, by sulphuric acid, or by chlorine. Tallow is added to increase the firmness of the soap. For yellow soap, resin is added to the palm oil.

Galam butter, from *Bassia butyracea*, is often confounded with palm oil. It is softer and more fusible, and is equally liable to rancidity.

There are some other kinds of vegetable butter, which, however, are too little known to be accurately described.

Tallow.—This name is given to the fat of oxen, sheep, deer, and goats. They all consist chiefly of stearine with a little oleine; but the last-named contains also caprine (caprate of oxide of glyceryle) in small quantity, to which it owes its peculiar smell. They form with soda firm hard soaps, and are much used, not only for soap-making, but for ointments and plasters, and in making candles. Tallow soon becomes rancid on exposure to the air. The fat of *ox-marrow*, having very little tendency to rancidity, is used for salves and pomatums.

Butter, derived from the milk of the cow, is a soft yellowish fat, which may be purified from buttermilk, cheese, and the other impurities it contains, by melting it, when the water subsides, and the pure oil rises to the surface. It should be repeatedly melted with water. It consists of margarine, oleine, butyrine, caproine, capryline, and caprine. The four latter are compounds of oxide of glyceryle with the volatile butyric, caproic, caprylic, and capric acids. Their quantity is small, but to them are owing the peculiar pleasant taste and smell of fresh butter. Butter soon becomes rancid: hence the necessity of either procuring it always fresh, or of salting it. When purified as above, it keeps much longer, but is much less pleasant to the taste. If melted butter be poured into ice-cold water, it assumes the consistence of fresh butter.

Rancid butter, like other rancid fats, may be in a great measure deprived of rancidity by melting and shaking it repeatedly with twice its weight of boiling water, which dissolves the free volatile oily acids, on the presence of which the rancidity depends. Fresh butter, when laid in syrup, keeps even better than salted butter.

Hog's-lard, or *Axunge*, is softer than tallow. It contains more oleine, and probably margarine, along with the stearine, or in place of it. It is chiefly used for ointments.

Human fat appears to contain no stearine, but only margarine and oleine.

Spermaceti.—This remarkable fat is found in certain cavernous receptacles in the head of several species of *Physeter* and *Delphinus*. During the life of the animal, it is dissolved in spermaceti oil; but, after death, it is deposited on cooling in a crystalline mass. It consists chiefly of cetine, which is contaminated with an oil soluble in cold alcohol.

Cetine.—To obtain it pure, spermaceti is dissolved in boiling alcohol, which on cooling deposits the cetine in crystals. The process is repeated as long as the alcohol extracts any oil. Pure cetine is crystalline, has a bright pearly lustre, and melts at 120° . At 670° it sublimes undecomposed. If distilled at a higher temperature, it yields inflammable gas, but is chiefly converted into ethalic or cetylic acid, and cetène, a liquid carbohydrogen of the formula $C_{32}H_{32}$: indeed, if the heat be carefully regulated, it may be entirely converted into these two products; but no ethal (hydrated oxide of cetylc) is formed.

When saponified by fusion with caustic potash, it yields cetylate of potash and ethal, (hydrated oxide of cetylc,) but no oleate or margarate of potash, as was formerly believed. According to L. Smith, purified spermaceti, or cetine, is pure cetylate of oxide of cetylc; and the oil formerly taken for oleic acid is not derived from the cetine, but from the spermaceti oil which accompanies it in the natural state, some of which adheres to it if not carefully purified. The formula of cetine is $C_{64}H_{64}O_4 = C_{32}H_{33}O + C_{32}H_{31}O_3 = CAO + \overline{Cet}$; that is, 1 eq. oxide of cetylc, and 1 eq. cetylic acid. This explains the products of its saponification and of its distillation. In the latter case, the ethal, $C_{32}H_{33}O$, losing 1 eq. of water, becomes cetène; while the cetylic acid, taking up that eq. of water, distils over as hydrated acid.

This view of the nature of cetine, although simple, is not to be considered as fully established; for, as Smith remarks, cetine has not the characters of a combination of an acid with a base. It differs from all other fats in not containing oxide of glycerylc or oxide of lipyle; and the extreme difficulty with which it is saponified seems to indicate that it does not contain cetylic acid ready formed, but that this acid and the ethal are first produced under the influence of the alkali at a high temperature. Viewed in this way, cetine is more analogous to cholesterine, ethal, and wax, than to the saponifiable fats. If we take half the above formula, namely $C_{32}H_{32}O_2$, then, when it is heated with potash, 1 eq. of cetine takes 2 eq. of oxygen from another eq., becoming hydrated cetylic acid, $C_{32}H_{32}O_4 = C_{32}H_{31}O_3 + HO$. The basic water is then replaced by potash, yielding cetylate of potash, $C_{32}H_{31}O_3, KO$; while the water unites with the carbon and hydrogen of the second eq. of cetine, forming ethal, $C_{32}H_{32} + HO = C_{32}H_{33}O$. Both views are equally con-

sistent with the qualitative and numerical results; the only difference is, that the first admits the existence of cetylic acid and of ethal ready formed in cetine, while the second regards them as products of decomposition.

When spermaceti is heated with nitric acid, it is slowly dissolved and oxidized. The acid liquid has a smell of rancid butter and train oil, and probably contains a little butyric, cœnanthylic, or valerianic acids. When evaporated it yields not a trace of suberic acid, but a large quantity of a crystallized acid, which, according to Smith, has all the properties of adipic acid, but a formula differing from that of Bro-meis ($C_{14}H_9O_7, 2HO$) by 1 eq. of hydrogen, namely, $C_{14}H_{12}O_9 = C_{14}H_{10}O_7, 2HO$. The acid mother-liquid of these crystals, when mixed with water, yields an oily liquid containing some acids not yet ascertained.

According to Radcliff, there is first produced pimelic acid, $C_7H_6O_4$. This is further oxidized into adipic acid, the formula of which he states to be $C_{14}H_{11}O_9, HO$; thus, $2(C_7H_6O_4) + O_2 = C_{14}H_{12}O_{10}$. By continued oxidation the adipic acid is converted into succinic acid; thus, $2(C_{14}H_{11}O_9) + O_{11} = 7(C_4H_3O_4) + HO$. The last formula is that of succinic acid.

Cholesterine or Fat of Bile.—This fat is found in the blood, the brain, and the bile of animals. It is the chief ingredient of biliary concretions, from which it is readily obtained by solution in boiling alcohol, which on cooling deposits the cholesterine, retaining in solution the small portion of colouring matter which it dissolves. Any fatty acids which may contaminate it are easily removed by potash.

It forms large pearly or silvery scales, insoluble in water, fusible at 279° , and volatilizable in close vessels, without change. It is not saponified nor dissolved by caustic alkalies; and it appears to be dissolved in the serum of the blood by means of soap, stearate of soda being present in that fluid. Wagner has shewn that 4 parts of soap, dissolved in water, take up one part of cholesterine.

The analyses of cholesterine, by Chevreul, Couerbe, and Marchand, indicate either the formula $C_{38}H_{33}O$ or $C_{36}H_{32}O$. A knowledge of its atomic weight can alone decide between these formulæ.

Cholesteric Acid.—By boiling with nitric acid, cholesterine is converted into cholesteric acid. This acid forms pale yellow needles, lighter than water, very soluble in ether. It forms red salts; those with the alkalies are soluble, the rest insoluble. Its formula is unknown, but it contains nitrogen, derived from the nitric acid. (Pellétier and Caventou.)

Ambreine.—This is a substance closely allied to cholesterine. It

occurs in ambergrise, a peculiar fat found floating on the sea in the southern latitudes, and supposed to be a concretion formed in the stomach of the spermaceti whale. From ambergrise ambreine is obtained, exactly as cholesterine is from biliary calculi. By the action of nitric acid it is converted into an acid, *ambreic acid*, analogous to cholesteric acid, and, like it, containing nitrogen.

Castorine.—This is a crystallizable substance, analogous to the two preceding, which is extracted, along with common fat, from castor (*castorcum*) by the action of alcohol. It dissolves unchanged in alkalis, and is converted by nitric acid into an acid analogous to ambreic acid. (Brandes.)

WAX.

This substance, or a substance closely resembling it, is found in many plants, particularly in the pollen. It is collected by bees to build their combs; but it is now ascertained that these animals possess the power of producing it from sugar,—a fact of much interest in reference to the origin of fatty matter in the animal organism.

As obtained by melting honeycomb with water, it is yellow, and has a peculiar smell. It melts at 145° . When exposed in thin layers, or ribbons, to the action of light, it is bleached, and deprived of smell. When bleached it melts at 158° , and congeals at 149° .

According to the researches of Gay-Lussac and Thenard, Chevreul, Saussure, Ettling, and others, wax is a mixture of two substances in very variable proportions. One of these is very soluble in hot alcohol, the other very sparingly soluble in that menstruum. The former is cerine, the latter myricine.

Cerine is deposited in a gelatinous mass, composed of fine needles, from the alcohol on cooling. When boiled with potash it is partially saponified, and the soap appears to contain margaric and oleic acids.(?) There is obtained at the same time about 56 p. c. of a neutral substance; insoluble, or nearly so, in alcohol, and unchanged by boiling with potash. This is *ceraine*. It seems to have the same composition as the portion of wax insoluble in alcohol.

Myricine.—This is the matter left undissolved when wax is boiled with alcohol. It requires 200 parts of boiling alcohol for solution, and is not affected by boiling with caustic potash.

The formulæ of these compounds are not ascertained; but the analyses of Ettling and Hess shew that cerine contains more oxygen than myricine; while the composition of ceraine and myricine appears to be the same.

Some species of vegetable wax appear to be composed of myricine

alone, others of cerine; while the so-called wax of *Myrica cerifera*, when saponified, yields stearic, margaric, and oleic acids, along with glycerine, and is therefore rather fat than wax. Bees' wax varies very much in the proportions of myricine and cerine which it contains.

When wax is distilled it yields a fatty acid, not yet examined; an oil composed of carbon and hydrogen in the same proportions as olefiant gas; and a solid white crystallizable substance of similar composition, which is identical with paraffine. Neither sebatic acid nor acroleine appears among the products. When wax is heated with nitric acid, it is almost entirely converted into succinic acid.

Japan or Tree Wax, from the fruit of *Rhus succedanea*, resembles wax in appearance, but, according to Sthamer, is really a fat identical in composition with the solid part of palm oil, palmitine. It contains no oleine, and is easily saponified, yielding palmitic, or perhaps palmitonic acid and glycerine. Heated with nitric acid, Japan wax yields succinic acid in large quantity, the formation of which is probably preceded, as in the case of spermaceti, by that of pimelic and adipic acids. Substances more or less similar to wax are obtained also from *Croton sebiferum*, *Celastrus ceriferus*, and *Ceroxylon andicola*. They are as yet little known.

Cerosine.—Some species of sugar-cane yield on the surface of the cane a wax-like substance, which has been examined by Dumas, who has given to it the above name. It forms fine light pearly scales, fusible at 180° , and is not saponified by potash. The analysis of it by Dumas led him to the formula $C_{48}H_{50}O_2$.

APPENDIX.

ORGANIC ACIDS, HITHERTO LITTLE EXAMINED.

Cainic Acid.—This acid occurs in the root of several species of *Chinococca*. Formula, $C_8H_7O_4$?. (Liebig.) It is crystallizable, and has at first little taste, but soon developes an acrid bitterness. It is sparingly soluble in water and ether, more soluble in alcohol.

Cramerie Acid.—This acid is found in rhatany root, said to be the root of *Crameria triandra*; but some commercial specimens do not yield it. It is crystallizable, soluble in water, and has a sour astringent taste. It is remarkable for its strong affinity to baryta. It is even capable of depriving sulphate of baryta of that earth; and the cramerate of baryta is not decomposed, either by sulphuric acid or by soluble sulphates. Its composition is unknown.

Caffeic and Tanno-caffeic Acids were discovered by Rungé in coffee. The former is a white powder, which when heated yields the aromatic odour of roasted coffee. It has recently been investigated by Rochleder, who finds its formula to be $C_{16}H_7O_6, 2HO$. The latter is a variety of tannic acid, producing in salts of iron a green precipitate.

Boletic Acid.—Discovered by Braconnot in the fungus *Boletus pseudo-igniarius*. It is crystallizable and volatile, and precipitates peroxide of iron completely from its solution.

Fungic Acid occurs, according to Braconnot, in most fungi. It does not crystallize, is deliquescent, and has a very sour taste.

There are several other acids, the existence of which as distinct compounds is still problematical: such are, Tanacetic Acid, in *Tanacetum vulgare*; Lactucic Acid, in *Lactuca virosa*; Atropic Acid, in *Atropa belladonna*; Cocognidic Acid, in the seeds of *Daphne gnidium*; Solanic Acid, in the different species of *Solanum*; Coneic Acid, in *Conium maculatum*; Aceric Acid, in *Acer campestre*; Moroxylic Acid, in the wood of the Mulberry; Kinovic Acid, in the Chinanova bark; Menispermic Acid, in *Cocculus indicus*, which is the seed of *Menispermum cocculus*.—an acid said to exist in the silkworm, &c. It is probable that most of these acids, when properly investigated, will be found identical with some one or other of the acids previously described.

OF THE VOLATILE OR ESSENTIAL OILS.

Many vegetable products, when distilled with water, yield essential or volatile oils, which are liquids, more or less volatile, sparingly soluble in water, generally colourless, although occasionally having a peculiar tint, and for the most part possessing the entire odour of the plant. They are inflammable, burning with a bright but smoky flame, and undergo peculiar changes by the action of air and water.

Analogous to these are the so-called empyreumatic oils, which are among the products of the destructive distillation of organic matter.

Many of the essential oils exist ready formed, and in the free state, in certain parts of plants; as, for example, in the rind of the orange and lemon, from which they may be obtained by mere pressure. Others flow from incisions in the plant, combined with resin, forming what are called Balsams; as is the case with oil of turpentine. In several cases it has been proved, that the oils are first formed by the mutual action of two or more organic compounds when the plant is placed in contact with water: this is the case with the oil of bitter almonds and with oil of mustard, and is true of all the volatile odoriferous oily matters formed during fermentation or putrefaction. (See ante, Amygdaline.)

It thus happens that perfectly inodorous plants, as, for example, *Centaurium minus*, when allowed to ferment with water, and then distilled, yield a penetrating essential oil.

The essential oil of *Spiræa ulmaria* may be obtained, with all its characteristic properties, from salicine, by the use of oxidizing agents, (see Hyduret of Salicylc ;) and, finally, when starch or saw-dust and similar substances are heated with sulphuric acid, peroxide of manganese, and water, they yield, besides formic and carbonic acids, oily liquids possessing all the characters of essential oils.

In some fragrant flowers, as the lime blossom, jonquil, and jasmine, the odorous principle may be extracted by ether or by fixed oil, but cannot be obtained by distillation with water; either because it is decomposed, or else is so soluble that it cannot be separated readily from the water. In the latter case, it may sometimes be separated by saturating the water with common salt.

Many essential oils contain a crystalline substance dissolved, to which the name of Stearoptène is given. This, in numerous cases, as in the oils of lavender and valerian, is pure camphor. Others contain volatile oily acids mixed with a neutral oil, as is the case in oil of cloves; and many contain nitrogenized compounds, such as ammonia and hydrocyanic acid.

Their specific gravity varies; some are heavier, others lighter than water.

Some contain no oxygen; while in others that element is present. It is worthy of especial notice, that a large proportion of the non-oxygenated essential oils as yet accurately analyzed contain carbon and hydrogen in the same relative proportions, expressed by the empirical formula $C_{10}H_8$. With widely different properties, they yield the same result, as to these elements, in 100 parts. There can be no doubt that in many cases the true formula is a multiple or submultiple of the above. In others, the arrangement of the same number of equivalents may vary.

The oxygenated essential oils are commonly mixtures of several, differing in volatility; but, as no one has succeeded as yet in effecting their complete separation in any case, the analyses of them which have been made are of no value.

All essential oils are miscible with alcohol; and they are more soluble in weak spirits, the more oxygen they contain. To water, although sparingly dissolved by that liquid, they give their peculiar odour, forming what are called *distilled waters*. When these are made by distilling the plant with water, they are apt to mould, from the presence

of foreign matter; but, if distilled a second time, they keep well in close vessels.

It must here be observed, that the odour of these oils is closely related to their alteration by air and water. They almost all absorb oxygen, and those which do so most rapidly have the strongest smell. If non-oxygenated oils be distilled with quicklime in vacuo, or in an atmosphere of carbonic acid, the product is absolutely inodorous; and it is impossible in this state to discriminate oil of lemons from oil of turpentine or of juniper: but, when exposed to the air, they quickly become odorous, while they absorb oxygen, becoming viscid and resinous. It would appear, therefore, as if the odour accompanied the act of oxidation, as is the case with metallic arsenic. By long exposure to the air, these oils gradually acquire the aspect of resins. Many become acid which before were neutral: the acid in oil of cinnamon is cinnamic acid; in oil of bitter almonds it is benzoic acid; and, according to Bizio, in some cases it is acetic acid. It is probable that the resins formed by the oxidation of essential oils are identical with those which in the balsams accompany the oils; but on this point we have no experiments. According to Saussure, carbonic acid is one of the products of the action of the atmosphere on essential oils.

It is not probable that these oils act as radicals, combining with oxygen directly to form the resins; it seems more likely that the oxygen removes one portion of their hydrogen, while the remainder of the hydrogen resists the action of oxygen, chlorine, and iodine much more strongly.

All the non-oxygenated oils, in contact with iodine, yield a part of their hydrogen with a kind of explosion, while iodine replaces the hydrogen thus removed. The new compound, although rich in hydrogen, does not yield any more to an additional quantity of iodine. The action of both oxygen and chlorine is analogous: both remove a part of the hydrogen; both also enter into the new compound, replacing that element: so that the new body, the resin, for example, always contains less hydrogen than the oil.

By strong nitric acid the essential oils are converted into resinous matters, as yet little studied. Many oils burst into flame when mixed with nitric acid, especially if a little sulphuric acid be previously added to it. When boiled with moderately strong nitric acid till dissolution ensues, the oils yield peculiar crystallizable acids, but no oxalic acid.

The essential oils dissolve sulphur and phosphorus, and are miscible with bisulphuret of carbon and hydrated acetic acid.

We shall now briefly describe the individual oils, and their relation to other substances. The whole subject is but imperfectly known;

and a profound and searching investigation is required, not only of their composition, but also and chiefly of the changes they undergo by the action of oxygen, chlorine, iodine, &c., before we can hope to acquire a knowledge of their true nature and constitution. Oil of turpentine and oil of lemons, for example, are both composed according to the empirical formula $C_{10}H_8$. The latter may be $C_{10}H_7 + H$; the former $C_{20}H_{15} + H$. It is obvious that the decision of these and similar questions cannot be expected from mere analyses of the oils, however accurate.

1. NON-OXYGENATED ESSENTIAL OILS.

Oil of Turpentine.—Turpentine, which is a semi-fluid mass, flowing from incisions in the wood of many species of *Pinus*, and which is a good type of the balsams, yields the oil in question when distilled with water. The oil of commerce, from exposure to the air, is always contaminated with resin. To purify it, it is again distilled with water, dried by chloride of calcium, and rectified. It is then clear, colourless, very mobile, and has a very pungent peculiar smell and a burning taste. Its sp. gr. is 0·86 to 0·87. When pure, it is neutral to test paper. It boils at 312° , and the density of its vapour is 4·764. (Dumas.) It is almost insoluble in water, but communicates to that liquid its smell. When moist, and left long in the cold, it often yields a solid crystalline hydrate, in which to $C_{10}H_8$ there are 2 at. water, (Blanchet and Sell,) or 3 at. (Dumas and Peligot.) This hydrate is soluble in 22 parts of hot water, and crystallizes on cooling. The oil is very soluble in alcohol, ether, and fixed oils. Being less soluble in weak spirits, it may be freed from resin by agitation with a little proof spirit.

It is instantly decomposed by sulphuric or nitric acid, and takes fire with a mixture of the two. Chlorine also acts on it rapidly, and with flame, if the quantity of oil be small in proportion to the gas. By the slow action of chlorine, one-fourth of the hydrogen is removed, and replaced by chlorine; and a similar effect is produced by bromine and iodine. It dissolves sulphur and phosphorus.

Pure oil of turpentine contains no oxygen. In 100 parts it is composed of

Carbon 88·46

Hydrogen 11·54,

which corresponds to the formula $C_{10}H_8$.

With hydrochloric acid gas it forms a liquid and a solid compound. The former is volatilizable, colourless, soluble in alcohol and ether. The vapour of this compound, passed over hot lime, yields chloride of calcium and an oil of the same composition as oil of turpentine. This

has been called Peucyl, or Peucylene. Its sp. gr. is 0·86, and it boils at 273°.

The solid compound may be purified by sublimation and crystallization from alcohol. It is white, translucent, lighter than water, insoluble in water, soluble in alcohol. Its solution does not precipitate nitrate of silver.

Its empirical formula is $C_{20}H_{17}Cl$. By repeated distillation of its alcoholic solution over hydrate of lime, the hydrochloric acid is at last removed; and it yields another oil of the composition of oil of turpentine, called Dadyl, Terebene, or Camphilene. Its sp. gr. is 0·86, and it boils about 300°. According to Dumas, who considers it to be pure oil of turpentine, and calls it Camphene, its true formula is $C_{20}H_{16}$, as deduced from the action of chlorine upon it. The results of Soubeiran and Capitaine, and of Deville, confirm this view.

The last-mentioned oil, when brought in contact with hydrochloric acid gas, reproduces the crystalline compound above mentioned, which has long been known as Artificial Camphor. According to Blanchet and Sell, oil of turpentine is a mixture of two oils, Peucyl and Dadyl, which have the same composition, and of which the former gives with hydrochloric acid a liquid, the latter a solid compound.

By the action of nitric acid, oil of turpentine is first converted into a resinous mass, which by long boiling with the acid is at last dissolved, and converted into a crystalline acid, *Terebinic acid*. According to Bromeis, its formula is $C_{14}H_9O_7, HO$. It merits a careful investigation.

Oil of turpentine is used in medicine both internally and externally. It is also much used in the arts for dissolving resins and oils in making varnishes.

Oil of Juniper.—Obtained from the berries of *Juniperus communis* by distillation with water. The unripe berries yield most oil; and this oil is a mixture of two, differing in volatility, as one boils at 310°, and the other at 400°. Both have the odour of juniper; and both, when agitated with a solution of salt, form crystalline hydrates. The more volatile portion has the same composition in 100 parts as oil of turpentine, and forms with hydrochloric acid gas a liquid compound, the formula of which appears to be $C_{15}H_{13}Cl$, according to Soubeiran and Capitaine, who call the supposed radical of this compound *Juniperilène*.

The addition of a little oil of juniper to brandy forms gin, or geneva. Both this and the oil are used as diuretics, and give to the urine the smell of violets.

Oil of Sabine, from the berries of *Juniperus Sabina*, resembles the

preceding, has the same composition, and is also used as a diuretic. Its smell, however, is disagreeable.

Oil of Elemi, from the resin of *Amyris elemifera* and *A. ceylanica*, is colourless, has a pleasant smell, the sp. gr. 0·852, and boils at 330°. Its other properties resemble those of oil of turpentine, except that it does not produce artificial camphor with hydrochloric acid gas, which colours it brown. It has the composition of oil of turpentine; and its formula is C_5H_4 , or a multiple of this.

Oil of Storax, obtained from *Storax liquida* by distillation with water, is colourless, and has the smell of the balsam. When purified it is called *Styrole*, and its formula has been ascertained to be $C_{16}H_8$. It is a very remarkable oil, and has been already described under cinnamic acid, from which it may be obtained by the action of heat.

Oil of Lemons, obtained by pressure from the peel of the fruit of *Citrus medica*, is generally yellowish and slightly turbid. When purified by rectification, it is clear, colourless, has a strong and pleasant smell of lemons, and a hot pungent taste. It has a sp. gr. of from 0·848 to 0·85 and higher, and boils from 330° to 353°, being a mixture of two oils, which may be separated by distillation to a certain extent. The more volatile portion is also the lighter of the two. Reagents act on it very much as on oil of turpentine; and, like that oil, it forms with hydrochloric acid gas a solid and a liquid compound, which both have exactly the same composition, but contain for the same amount of carbon and hydrogen twice as much hydrochloric acid as the corresponding compounds of oil of turpentine. When deprived of the hydrochloric acid by quicklime, they yield two oils of the same composition: one of which, *Citrène*, has the sp. gr. 0·847, and boils at 330°; the other, *Citrilène*, has the sp. gr. 0·88, and boils at 345° to 353°. It is the former, *Citrène*, that yields the solid compound with hydrochloric acid. (Blanchet and Sell, Soubeiran and Capitaine, Dumas.)

Both oil of lemons and the two oils last described have the composition, in 100 parts, of oil of turpentine; and the formula $C_{10}H_8$, or more probably C_5H_4 . The crystalline compound with hydrochloric acid seems to be $C_{10}H_9Cl$.

The *Oils of Cedro* and *Cedrat* are probably identical, when pure, with oil of lemons.

Oil of Oranges, from orange-peel, *Citrus aurantium*, differs only in smell from oil of lemons. Its composition and its actions with reagents are precisely the same.

Oil of Neroli, or of orange-flower, is quite distinct from the above oils, which are derived from the fruit. It has the peculiar fragrance of the flowers, and is in great part soluble in water; it is soon reddened

by the action of air and light. Orange-flower water is a solution of this oil, obtained by distilling the flowers with water. Oil of neroli appears to contain a stearoptène, possibly a hydrate. The composition of the oil is not exactly known, and it is doubtful whether it contain oxygen or not.

Oil of Copaiva, obtained by distilling balsam of copaiva (from *Copaifera multijuga*) with water, is colourless, has the sp. gr. 0·91, and boils at 473°. It is soluble in $2\frac{1}{2}$ parts of absolute alcohol; but requires 25 to 30 parts of alcohol, sp. gr. 0·85, for solution. Reagents act on it as on oil of turpentine. Nitric acid causes a kind of explosion; producing a crystalline compound; at first yellow, then blue, and finally becoming green. With hydrochloric acid it forms a crystalline compound, having the composition of that from oil of lemons, $C_{10}H_9Cl$; it also forms a liquid compound: but the radicals of these could not be isolated. (Soubeiran and Capitaine, Blanchet.) The oil of copaiva has the same composition as oil of turpentine. It is used in medicine.

Oil of Pepper, from *Piper nigrum*, has similar properties and the same composition; but it does not form a crystalline compound with hydrochloric acid, which it absorbs in large quantity.

Oil of Cubebs, from the fruit of *Piper cubeba*, is colourless and aromatic, sp. gr. 0·929, boils at about 490°. It gives a crystalline compound with hydrochloric acid, which seems to be $C_{15}H_{13}Cl$. The oil is supposed by Soubeiran and Capitaine to be $C_{15}H_{12}$, which is still the same in 100 parts as oil of turpentine.

OXYGENATED ESSENTIAL OILS.

Oil of Bitter Almonds, obtained by distilling with water the bruised almonds after the fixed oil has been expressed, is yellow, and has a pleasant smell and a hot taste. It is a mixture of hyduret of benzoyle with hydrocyanic acid, both formed by the mutual action of amygdaline, emulsine or synaptase, and water. It is very poisonous. (See Benzoyle and its compounds.)

Oil of Laurel leaves, obtained by distilling the leaves of *Prunus laurocerasus* with water, appears to be essentially the same as oil of bitter almonds.

The leaves and kernels of the peach, *Amygdalus persica*, and of *Prunus padus*, as well as other species of *Amygdalus* and *Prunus*, yield a similar oil.

Oil of Spiræa. (See Salicylc and its compounds.)

Oil of Wintergreen, from *Gaultheria procumbens*, is the salicylate

of oxide of methyle. It is very fragrant, and has acid properties so far as to combine as a whole with bases, forming salts, which are called *Gaultherates*. When boiled with alkalis, it yields salicylates and hydrated oxide of methyle. Nitric acid converts it into crystallized anilate of oxide of methyle, and, with the aid of heat, into nitropicric acid. This oil is isomeric with anisic acid; for $C_2H_3O + C_{14}H_5O_5 = C_{16}H_7O_5.HO$. Both substances, when heated with baryta, yield anisole.

Oil of Cinnamon.—Of this oil there are two varieties: Ceylon oil of cinnamon, from *Laurus cinnamomum*, and common oil of cinnamon, from *Laurus cassia*. Both, when fresh, are pale yellow, but become brown on exposure to the air. They have a sweetish, pungent, aromatic taste, and a pleasant smell. Their sp. gr. is from 1.03 to 1.09. (See Cinnamyle and its compounds.) According to Mulder, both oils have the same composition, and the formula $C_{20}H_{11}O_2$, when quite fresh. On exposure to the air, they rapidly absorb oxygen, and produce cinnamic acid, two resins, and water. Mulder has analyzed both the resins, which he calls resin alpha and resin beta. The former is soluble in cold alcohol, and its formula is $C_{15}H_{7\frac{1}{2}}O_2$?. The latter is insoluble in cold alcohol, and has the formula $C_{12}H_5O$. If we compare the composition of these resins and of cinnamic acid with that of the oil, we find that 3 at. of oil of cinnamon $= C_{60}H_{33}O_6 + 8$ at. oxygen $=$

$$C_{60}H_{33}O_{14} = \begin{cases} 1 \text{ at. Cinnamic Acid} = C_{15}H_{7\frac{1}{2}}O_3 \\ 1 \text{ at. Resin Beta} = C_{12}H_5O \\ 2 \text{ at. Resin Alpha} = C_{30}H_{15}O_4 \\ 6 \text{ at. Water} = H_6O_6 \end{cases}$$

$$C_{60}H_{33}O_{14}$$

The 8 atoms of oxygen are derived from the air. Oil of cinnamon is decomposed by hydrochloric acid gas, yielding a volatile oil not yet examined, water, and two resins, one soluble, the other insoluble in cold alcohol. The formula of the latter is $C_{20}H_8O$; that of the former $C_{14}H_7O$. In like manner, concentrated sulphuric acid acts on the oil, producing two resins, one soluble, the other insoluble, in alcohol. The composition of the

former is	.	.	.	.	$C_{30}H_{15}O_2$, or
that of the latter	.	.	.	.	$C_{30}H_{15}O$
Together	.	.	.	.	$C_{60}H_{30}O_3$; which is

3 at. oil of cinnamon — 3 at. water. The sulphuric acid removes an atom of water from each atom of the oil, and the oxygen of the residue is unequally divided between the resins.

With nitric acid, oil of cinnamon forms a white crystalline com-

pound, $C_{18}H_9NO_7$. The oil $C_{20}H_{11}O_2$ loses here C_2H_2 , and takes up NO_5 , and the rational formula of the resulting compound is probably $C_{18}H_8O_3 + NO_3 + HO$, which explains its decomposition by contact with water, and the formation of cinnamic acid when it is dissolved in sulphuric acid. With water it yields an oil which is $C_{18}H_8O_2$, that is, hyduret of cinnamyle; while its solution in sulphuric acid, when mixed with water, deposits cinnamic acid, $C_{18}H_7O_3$.

Along with the crystalline compound, nitric acid produces a red oil, which is instantly decomposed by water, although not by anhydrous alcohol or ether. With water the red oil yields another oil, the formula of which is $C_{15}H_7O_2$. These results are taken from a recent memoir by Mulder.

Oil of Cloves.—From the undeveloped buds of *Caryophyllus aromaticus*. Sp. gr. 1·055. It is the least volatile of the essential oils, and is a mixture of caryophyllic acid and an indifferent or neutral oil. (See Caryophyllic Acid.)

Oil of Sassafras.—From *Laurus Sassafras*. Sp. gr. 1·08 to 1·09. It is coloured scarlet by nitric acid, yielding oxalic acid. When long kept, it deposits a stearoptène in large crystals, which melts in the heat of the hand, and is volatile.

Oil of Sweet Bay.—From *Laurus nobilis*. A dirty white, thick oil, with a pungent smell and a bitter taste. Sp. gr. 0·914. By distillation it yields a lighter oil, sp. gr. 0·857, and one less volatile, sp. gr. 0·885, while a thick mass remains in the retort. The more volatile portion, according to Brandes, has the formula $C_{20}H_{16}O$, which is that of the oil of camphor.

Laurine is a crystalline substance which may be extracted from bay leaves by absolute alcohol. It is fusible and volatile, and seems to be a neutral substance.

Some other oils, little known, are derived from different species of *Laurus* and *Persea*, such as *Laurus Pichurim*, *Laurus Culilaban*, &c.

Oil of Saffron.—From the stigmata of *Crocus sativus*. It is yellow, heavier than water, and gradually changes into a white solid, lighter than water. It has the odour of saffron.

Oil of Bergamot.—This oil, from *Citrus Limetta* (the lime), and *Citrus Bergamotta* (the bergamot), has an odour resembling that of oil of lemons, from which, however, it differs in containing oxygen. It is believed to contain a mixture of oils, having the composition of citrène, with a hydrate of such an oil, and an oxygenated oil formed by the action of the atmosphere. It generally deposits a stearoptène, which Ohme calls Bergaptène; the formula of which, according to Ohme and Mulder, is C_3HO . According to Soubeiran and Capitaine, anhydrous

phosphoric acid deprives the hydrate of its water, and the oil which separates has the composition of oil of lemons. A part of the oil seems to combine with phosphoric acid, producing an acid analogous to phosphovinic acid. With hydrochloric acid gas, oil of bergamot forms only a liquid compound.

Oil of Roses.—Otto or Attar of Roses, from the petals of *Rosa centifolia*, *moschata*, *sempervirens*, and other species. A yellowish thick oil, congealing in the cold to a buttery mass, composed of shining foliaceous crystals. When much diluted, its smell is highly agreeable; when strong, it causes headache. It has a mild aromatic taste, sp. gr. 0.832. It consists of a solid (stearoptène) and a liquid oil, in variable proportions. The solid portion, which is insoluble in alcohol, and may be purified by solution in ether, has the formula CH , or some multiple of it.

Oil of Rhodium, from the wood of *Convolvulus scoparius*, has an odour of roses, and is sometimes used to adulterate oil of roses.

Oil of Rose Geranium, from *Pelargonium radula*, has also a similar odour, and is used for the same purpose; but it smells also of *Geranium Robertianum*. It is crystalline, and melts at 68° .

Oil of Cajeput, from *Melaleuca Leucodendron* and *Melaleuca Cajeputi*. It has commonly a pale green colour. Its odour is unpleasant, except when much diluted, when it resembles that of camphor and rosemary; sp. gr. 0.978. The green colour is natural to the oil, but is sometimes increased by the presence of copper, derived from the vessels in which it is kept. Blanchet and Sell found the composition of a very pure specimen to be $\text{C}_{10}\text{H}_9\text{O}$.

The *Oils of Nutmeg and Mace*, the former from the nut of *Myristica moschata*, the latter from the rind of the same nut, appear to be identical. They contain a liquid oil and a stearoptène. The latter, according to Mulder, is $\text{C}_8\text{H}_{16}\text{O}_3$.

Oil of Cardamom, from *Anomum repens*, belongs to this class of oils, but has not been minutely studied. It is aromatic, and its sp. gr. is 0.945.

The *Stearoptène of the Tonka Bean*, the fruit of *Dipterix odorata*, has a pleasant aromatic odour, is heavier than water, soluble in alcohol and ether, and crystallizable. It is called Cumarine, and its formula is $\text{C}_{18}\text{H}_6\text{O}_4$. The same compound occurs in Woodruff, (*Asperula odorata*), the aromatic fragrance of which is so well known, and in the fragrant grass *Anthoxanthum odoratum*.

Cumarine, when gently heated with hydrate of potash, takes up 2 eq. of water, one of which becomes basic, and yields a new acid, *cumaric acid*, $\text{C}_{18}\text{H}_8\text{O}_6 = \text{C}_{18}\text{H}_7\text{O}_5, \text{HO}$. This acid, when more strongly heated

with potash, is converted into salicylic acid, carbonic acid, and hydrogen, which escapes. $C_{18}H_8O_6 + 8HO = C_{14}H_5O_5, HO + 4CO_2 + 10H$.

By nitric acid cumarine is converted into *nitrocumarine*, $C_{18}\left\{\begin{smallmatrix} H_5 \\ NO_4 \end{smallmatrix}\right\}O_4$.

Oil of Anise, from *Pimpinella anisum*, is solid at temperatures below 50° , owing to the crystallization of a stearoptène which it contains in large quantity. The solid portion, according to Cahours, has the formula $C_{20}H_{12}O_2$. With chlorine it forms a liquid compound, $C_{20}H_9Cl_3O_2$; with diluted nitric acid it yields anisic acid, the compound of which with oxide of silver is $C_{16}H_7O_5, AgO$; and with fuming nitric acid another, the silver salt of which is $C_{16}H_7(NO_4)O_5, AgO$. Fused with hydrate of potash, it yields an acid, not further investigated. It also forms with sulphuric acid a solid compound, anisoine, isomeric with hyduret of anisyle; and with fuming sulphuric acid another new acid, which yields a soluble salt with baryta. (See Anisyle.)

Oil of Dill, from *Anethum* or *Apium graveolens*, has the strong smell of the plant, and a sweetish burning taste; sp. gr. 0.881.

Oil of Fennel, from *Anethum fœniculum*, has the odour of fennel, and the sp. gr. 0.997. It contains a stearoptène, which is the same as that of oil of anise. The difference between the two oils depends on the liquid portion.

Oil of Estragon, from *Artemisia dracunculus*, is identical with oil of anise; and the draconic acid, obtained from it by Laurent, is anisic acid.

The *Oil of Water Fennel*, from *Phellandrius aquaticus*, appears to contain ammonia, and is poisonous.

Oil of Parsley, from *Apium petroselinum*, has a strong smell of parsley, and contains a liquid and a solid portion. The former appears to have the composition of oil of turpentine; the latter is said by Loe-wig and Weidmann to be $C_{12}H_8O_3$.

Oil of Carraway, from *Carum carui*, appears to contain two oils differing in volatility. The more volatile seems to contain no oxygen; the other appears to be analogous to *oil of cumine*. (See Cuminic Acid.) The latter is derived from *Cuminum cyminum*.

Oil of Coriander, from *Coriandrum sativum*, has the smell of the seeds, and the very low sp. gr. of 0.759.

Oil of Pimpernel, from *Pimpinella saxifraga*, has a golden yellow colour, an unpleasant smell of parsley, and is lighter than water. That from *P. magna* is at first blue, then green.

Oil of Peppermint, from *Mentha piperita*, has commonly a pale yellow or green colour, and a pungent cooling taste. Its sp. gr. is 0.902 to 0.91. The American oil contains a stearoptène, which appears to

be $C_{10}H_{10}O$. (Dumas, Blanchet and Sell.) According to Walter, this should be doubled, $C_{20}H_{20}O_2$; and by the action of anhydrous phosphoric or sulphuric acid 2 at. of water are removed, and a carbo-hydrogen is left $= C_{20}H_{18}$, which Walter calls Menthene: so that the rational formula of the stearoptène is $C_{20}H_{18}, 2HO$, or possibly $C_{20}H_{19}O, HO$. Treated with chloride of phosphorus, the stearoptène yields chloride of menthene $= C_{20}H_{17}Cl$. Chlorine gas produces two other compounds containing chlorine.

By the action of nitric acid, menthene yields a compound, $C_{10}H_9O_9$; and by the action of chlorine it is converted into another compound, $C_{20}H_{13}O_5$. (Walter.)

Oil of Pennyroyal, from *Mentha pulegium*, has, according to Kane, the formula $C_{10}H_8O$; which is remarkable, as being identical with that of camphor.

The *Oil of Mentha viridis*, according to Kane, is $C_{35}H_{28}O$.

Oil of Marjoram, from *Origanum majorana*, contains a stearoptène, which, according to Mulder, is $C_{14}H_{15}O_5$. The oils of *Origanum Smyrnæum* and of *Origanum vulgare* are similar, and are used to adulterate the oil of marjoram. According to Kane, the latter is $C_{50}H_{40}O$.

Oil of Lavender, from *Lavandula spica*, has the odour of the plant, the sp. gr. 0·872, and boils at 365° . It contains a variable quantity of stearoptène, which, according to Dumas, is camphor.

Oil of Rosemary, from *Rosemarinus officinalis*, according to Kane, is $C_{40}H_{36} + 2HO$. Sulphuric acid blackens it, and causes the separation of an oil, having an alliaceous smell, and the composition of oil of turpentine. Kane calls this oil Rosmarine.

Oil of Basil, from *Ocimum basilicum*, contains a stearoptène, which Dumas and Péligot found to be $C_{20}H_{16} + 6HO$, agreeing in composition with the hydrate of oil of turpentine. The liquid portion has not been examined.

Oil of Thyme, from *Thymus vulgaris*, has the odour of the plant, and deposits a stearoptène when kept.

Oil of Valerian, from *Valeriana officinalis*, contains valerianic acid (see that acid) and a stearoptène.

Oil of Rue, from *Ruta graveolens*, is yellow or greenish, has the sp. gr. 0·837, and boils at a temperature from 425° to 473° . According to Will, its composition is $C_{28}H_{28}O_3$, and the density of its vapour, = 7·69, agrees with this formula.

Oil of Cascarilla, from the bark of *Croton eleutherium*, is sometimes yellow, at other times blue or green; has the sp. gr. 0·938; and contains two oils, one boiling at 344° , the other less volatile. According to Völckel, the former contains no oxygen, and has probably the

usual composition of non-oxygenated essential oils. The latter contains oxygen.

Oil of Chamomile, from *Matricaria chamomilla*, is dark blue, viscid, and has a bitter aromatic taste; sp. gr. 0.924. Nitric acid decomposes it, and the addition of water to the acid solution precipitates a resin having the odour of musk. It dissolves iodine without producing heat, unless when adulterated with oil of turpentine or of lemons, when the violent action of iodine on these oils discovers the adulteration. The Roman oil of chamomile, from *Anthemis nobilis*, is very similar to the above.

Oil of Wormwood, from *Artemisia absinthium*, is greenish yellow, has an unpleasant bitter taste, and the sp. gr. 0.897.

Oil of Tea, from *Thea viridis*, is yellow, and readily solidified by cold. It has the odour of tea in so high a degree that it is apt to cause stupefaction when smelt. In the process of drying the tea leaves, the greater part of the oil is lost, so that the best Hyson yields hardly 1 p. c. of the oil.

The following vegetables yield oxygenated essential oils, of which, however, so little is known, that for the present we merely give the catalogue of the names. Many of them contain stearoptène or solid volatile oils.

Teucrium marum, *Hyssopus officinalis*, *Salvia officinalis*, *Lycopus europæus*, *Ledum palustre*, *Achillea millefolium*, *Artemisia contra*, *Artemisia vulgaris*, *Tanacetum vulgare*, *Juniperus lycia* and *thurifera*, *Balsamodendron myrrha*, *Galbanum officinale*, *Ferula persica*, *Cupressus sempervirens*, *Thuja occidentalis*, *Aristolochia serpentaria*, *Cæsalpina crista*, *Hedwigia balsamifera*, *Betula alba*, *Wintera aromatica*, *Populus nigra*, *Chenopodium ambrosioides*, *Dahlia pinnata*, *Parmelia parietina*, *Tilia europæa*, *Sambucus nigra*, *Reseda odorata*, *Philadelphus coronarius*, *Jasminum officinale*, *Syringa vulgaris*, *Convallaria majalis*, *Diosma crenata*, *Myrica gale*, and others.

ESSENTIAL OILS CONTAINING SULPHUR.

Several essential oils contain sulphur; and, like all organic compounds in which sulphur is present in any form but that of its compounds with oxygen, they have generally a fœtid smell.

Oil of Mustard is obtained from the seeds of *Sinapis nigra*, exactly as oil of bitter almonds from that fruit. The seeds, deprived of fixed oil by pressure, are made into a paste with water, and this after some hours is distilled. The oil is not ready formed in the seed, but is produced by the mutual action of substances contained in them along with water.

Oil of mustard has the sp. gr. 1.038, is very pungent to the taste and smell. It contains sulphur and nitrogen: formula $C_8H_5NS_2$. When heated with potash it yields ammonia, sulphuret of potassium, and sulphocyanide of potassium. With ammonia it yields a white crystalline compound, which appears to be composed of $C_8H_5N_2S_2$, or $C_8H_5NS_2 + NH_3$. Will has minutely investigated the oil of mustard, and has confirmed the above formula. By the researches of Wertheim, it appears that oil of mustard is the sulphocyanide of allyle, a radical formerly mentioned. Allyle is C_6H_5 , sulphocyanogen is C_2NS_2 ; and $C_6H_5, C_2NS_2 = C_8H_5NS_2 = All, CyS_2$. When heated with sulphuret of potassium, KS, oil of mustard yields sulphocyanide of potassium, and sulphuret of allyle, or oil of garlic.

The compound above mentioned with ammonia has, according to Will, the characters of a base. He calls it *Thiosinamine*; and he has shewn that when acted on by oxide of lead or mercury, it loses all its sulphur, and part of its hydrogen, and yields another base, *Sinamine*, the formula of which is $C_8H_6N_2$.

When oil of mustard, or sulphocyanide of allyle, is acted on by oxide of lead, it yields a third base, *Sinapoline*. These bases will be described under the head of Organic Bases.

When oil of mustard is acted on by an alcoholic solution of potash, it yields 1 eq. each of carbonic acid, ammonia, an oily compound, $C_{28}H_{25}N_3S_4O_4$, and 2 eq. of a salt composed of potash with a new acid, $C_8H_5NS_2, HS$, which contains the elements of oil of mustard and sulphuretted hydrogen. These products are derived from 6 eq. of oil of mustard, 10 of water, and 2 of potash.

Both black and white mustard, according to Bussy, contain a substance analogous to emulsine or synaptase, called by him Myrosine; and an acid, Myronic acid, which, by the contact of myrosine and water, yields the oil of mustard, with other products not yet investigated. Myronic acid occurs in the seeds combined with potash, and the myronate of potash is the substance described by Henry and Garot as Sulphosinapine. It is remarkable that white mustard, although containing myrosine, which is identical with that of black mustard, and apparently also myronic acid, does not yield with water the oil of mustard, but another pungent oil. But the myrosine of white mustard, when added to the residue of black mustard deprived of its myrosine, yields the oil, just as the emulsine of sweet almonds acts on the amygdaline of bitter almonds.

It is obvious that the white mustard must contain a substance differing from myronic acid, else it would yield the same oil as black mustard; but this point is still very obscure, and Bussy has not yet

published his analysis of myronic acid, which contains carbon, hydrogen, nitrogen, oxygen, and sulphur. It forms salts which have a bitter taste and no smell. These salts, as well as the acid itself, when distilled with myrosine and water, yield the volatile oil. Some of them are crystallisable.

Besides myronic acid and myrosine, black mustard may be made to yield a neutral crystalline body, discovered by Simon, who calls it Sinapisine. It is obtained by digesting the seeds in strong alcohol, and acting on the alcoholic extract with ether. Its properties resemble those of the unsaponifiable crystalline fats. If the seeds, after the action of the alcohol, be digested with carbonate of soda, and the solution distilled with an excess of sulphuric acid, there is obtained a volatile acid, not unlike acetic or formic acid. Its salts are extremely soluble, and difficultly crystallizable. Both these compounds require a minute investigation.

Oil of Horseradish, from *Cochlearia armoracia* and *C. officinalis*, has a very pungent taste and strong smell. It contains sulphur, and causes blisters when applied to the skin. It has lately been shewn to be identical with oil of mustard. (Hubatka.)

Oil of Alliaria officinalis is also identical with oil of mustard. (Wertheim.) The leaves of this plant contain oil of garlic.

Oil of Garlic, from *Allium sativum*, has the smell of the plant, and smarts the skin when applied to it. It has been shewn by Wertheim to be the sulphuret of allyle, $C_6H_5S=AlS$. This compound unites with the sulphurets of several metals, forming double sulphurets. Some of these again unite with chlorides. Wertheim also obtained compounds of oxide of allyle with metallic nitrates.

The onion, *Allium cepa*, yields a similar oil.

Oil of Assafoetida, from *Ferula assafoetida*, has a still more offensive smell, and a taste at first mild, afterwards acrid. When rubbed with mercury it forms sulphuret of mercury. It appears to contain two oils, one of which, according to Douglas MacLagan, is sulphuret of allyle.

The oils of water-pepper (*Polygonum hydropiper*) and of *Arum maculatum* also belong to this class; as do those of *Lepidium latifolium* and of hops, (*Humulus lupulus*.)

APPENDIX TO THE ESSENTIAL OILS.

It is proper to mention here several substances which resemble the stearoptènes in so far as they are volatile, with few exceptions crystalline, and may be distilled along with the vapour of water.

Helenine, from *Inula Helenium*, may be obtained by acting on the fresh root with hot alcohol, or by distilling it with water. It crystallizes in white prisms, soluble in alcohol, ether, and essential oils, but insoluble in water. It melts at 162° , and boils about 530° . According to Dumas, its formula is $C_{14}H_9O_2$; according to Gerhardt, it is $C_{15}H_{10}O_2$. When helenine is heated with nitric acid till the product is entirely soluble in ammonia, and the solution mixed with water, there is precipitated a peculiar substance, nitro-helenine, which appears to be $C_{15}H_9O_2 + NO_4$. (Gerhardt.) With chlorine it yields chloride of helenine, $C_{15}H_{10}O_2 + Cl_2$; and Gerhardt obtained another substance, apparently a compound of this last with hydrochloric acid. Both are yellow powders. The latter, heated with quicklime, yields naphthaline. With anhydrous phosphoric acid, helenine yields a carbo-hydrogen, helenène, $= C_{15}H_8$, which is helenine — 2 at. water. With sulphuric acid, helenine forms a new acid, which, on account of its easy spontaneous decomposition, could not be examined.

Asarone, obtained by distilling the root of *Asarum europæum* with water, is a crystallized solid, with an aromatic taste and smell like those of camphor, fusible in boiling water, and softened by the heat of the hand. Its sp. gr. is 0.95. It sublimes unchanged when heated to about 570° . Its formula, according to Blanchet and Sell, is $C_{16}H_{11}O_4$; and these chemists consider it as the hydrate of an oil contained in the root, which they extracted by means of absolute alcohol. Their analysis of the oil, however, does not agree with this view. According to Schimdt, asarone passes easily into an isomeric modification of totally different properties. The new body is resinous, and neither volatile nor crystallizable; but if distilled with water it passes over in oily drops, which after a time crystallize. Asarone offers a most beautiful example of crystallization. Under the microscope, the fluid particles may be seen arranging themselves to form the crystals, and their motions and attractions admit of being studied. The isomeric change above mentioned is analogous to that which occurs in styrole when heated.

Nicotianine is a fatty substance, obtained in minute quantity by distilling tobacco leaves with water. It is insoluble in water; soluble in alcohol, ether, and potash. It has a bitter taste, and a strong smell of tobacco.

Anemonine occurs in *Anemone pulsatilla*, *nemorosa*, and *pratensis*. It is crystalline, heavier than water, and, when heated in a current of air, sublimes with a pungent acrid smell, but cannot be distilled unchanged in close vessels. According to Löwig, its formula is $C_7H_3O_4$. He found it soluble in ether. But Fehling states that it is very

sparingly soluble in that menstruum, and soluble in hot alcohol. Four analyses by Fehling give the formula $C_5H_2O_2$. By boiling it with oxide of lead and water he obtained a compound which seems to be $C_{15}H_6O_6, PbO$. By the action of baryta Löwig obtained an acid, Anemonic acid, the formula of which he states to be $C_7H_4O_3, HO$.

The pods of *Epidendron Vanilla* yield a crystalline body in soft needles; and the wood of *Quassia amara* also contains a crystalline body. Neither of these has been much studied. The seeds of *Tanghinia madagascariensis* yield to ether a crystalline substance, which is highly poisonous.

According to Bonastre, Massey bark contains a camphor-like substance, along with two volatile oils.

Hünefeldt has shewn that the root of *Primula auricula* contains a volatile crystalline body, which has an odour resembling that of pepper-mint; and that the root of *Primula veris* yields another, which smells like fennel and garlic. He calls them Auricula camphor and Primrose camphor.

Cantharadine is a volatile crystalline body, contained in the insects *Lytta ruficollis*, *L. gigas*, and *L. vittata*. It is very soluble in ether, alcohol, and essential oils, and is volatile. It is the source of the blistering power of the insects. Regnault found it to be composed of $C_{10}H_6O_4$.

CAOUTCHOUC.

This remarkable substance, which has some analogy with the resins, occurs in the form of bottles, which are made by allowing the juice of the trees which yield it to flow from incisions on shapes of unburnt clay, which are broken when the caoutchouc has attained a sufficient thickness.

Caoutchouc is obtained from several trees, both in Asia and America, and particularly from *Siphonia elastica*, *Tabernamontana elastica*, and *Lobelia caoutchouc*. The former has been variously named, and is known as *Jatropha elastica*, *Hevea guianensis*, *Siphonia cahuchu*. The second-named plant, *Tabernamontana*, has also been named *Urceola elastica*. Several species of *Ficus*, and many other plants, contain it likewise.

The juice is sometimes imported in closely stopped vessels. It is yellowish and thick, like cream, and has a sour smell, arising from the putrefaction of the vegetable albumen it contains. This albumen is coagulated by heat, and thereby causes the separation of the suspended caoutchouc. According to Faraday, the juice contains, in 100 parts 32 of caoutchouc, 2 of vegetable albumen, 7 of a nitrogenized sub-

stance soluble in water, 3 of a substance insoluble in water, and 56 of water.

Pure caoutchouc is transparent and colourless, the black colour of the commercial article being derived from the smoke in which it is dried. It is perfectly elastic, and when suddenly stretched, gives out much heat and free electricity. It is a nonconductor of electricity. When it has once separated from the juice in the solid form, there is no method known of obtaining it again suspended as before. In hot water it swells and becomes soft, but is utterly insoluble both in water and alcohol. Pure ether dissolves it, and leaves it by evaporation in a perfectly elastic state, and with a surface like that obtained by cutting it, when it has the property of adhering firmly to another similar surface, if the two be strongly pressed together. This property enables us to form tubes from a plate of caoutchouc by folding it round a cylinder, cutting off the superfluous edges with a clean and sharp pair of scissors, and then pressing together the fresh cut edges. Tubes thus made are perfectly air and water tight. In rectified naphtha from wood or coal tar, caoutchouc is soluble; and the water-proof cloth of Mackintosh is made with a viscid solution in a mixture of oil of turpentine and coal-naphtha, the solvent being removed by evaporation in chambers heated by steam, and leaving the caoutchouc with all its properties. Essential oils will also dissolve it alone; but, from the presence in them of resin, which remains after evaporation of the oil, the caoutchouc does not dry properly, but remains viscid.

Heated to 248° , it melts, and continues long viscid and soft. In this state it may be used as a luting, where a high temperature is not employed.

When more strongly heated, it is decomposed, and the greater part distils over in the form of a mixture of oily liquids. These differ extremely in volatility; the most volatile portion boiling about 90° , the least volatile at 680° , and the greater portion at intermediate temperatures. According to Himly, all these oils have the empirical formula C_5H_4 , which is that of oil of turpentine. Gregory found a portion which boiled at 97° to have very nearly the composition of olefiant gas, C_2H_2 ; and, when this oil was acted on by sulphuric acid, it blackened, gave off sulphurous acid, and, on the addition of water, yielded an oil which boiled at a temperature above 428° , but still having the same composition.

By careful rectification Himly obtained an oil, the boiling point of which was constant at 339° , which he calls *Caoutchine*. It had the composition of oil of turpentine. Bouchardat, by applying an intense cold to the receiver, obtained a liquid, *Caoutchène*, which boiled be-

low 32° , and is probably identical with Faraday's quadricarburetted hydrogen, C_4H_4 . He also analysed another oil, *Hévène*, boiling at 599° , which had the same composition. From the experiments of Himly, Bouchardat, and Gregory, therefore, it appears that caoutchouc by distillation yields many oily liquids, some of which have the composition of olefant gas, and others that of oil of turpentine. Gregory's volatile liquid above mentioned had the very low sp. gr. of 0.654. Himly's caoutchine had the sp. gr. 0.842.

The purest caoutchouc that Faraday could obtain from the juice was found by him to contain 87.2 p. c. of carbon, and 12.8 p. c. of hydrogen.

RESINS.

This class of compounds occurs almost exclusively among vegetables. They either flow from them dissolved in essential oils, forming balsams, or are found deposited in the wood. What are called fossil resins are doubtless derived from extinct vegetation.

There is a close connexion between resins and the oils in which they occur dissolved. All resins contain oxygen, and most essential oils become resinous by the absorption of oxygen from the air. It is not, however, probable that resins are merely the oxides of essential oils. From the fact that iodine, a substance which has a very feeble attraction for hydrogen, acts strongly on essential oils, depriving them of a part of their hydrogen, it is obvious that that portion of hydrogen is in a different state of combination from the remainder; and it is most probable that the oxygen of the air removes this loosely combined hydrogen, forming water, while oxygen also replaces the hydrogen which has been removed. The water thus formed may either remain in combination with the new oxidized compound, or be separated.

Hence, when an essential oil is converted into resin by exposure to the air, the composition of the resin must be equal to that of the oil, *minus* a certain quantity of hydrogen, and *plus* a certain quantity of oxygen.

This appears to be the relation between common resin and oil of turpentine, and between the resin and oil of copaiva. Both of the oils are C_5H_4 or $C_{10}H_8$; and the resins are $C_{10}H_7O$, or, if we adopt the atomic weights as found by Rose, $C_{40}H_{28}O_4$. Here $C_{40}H_{32}$ have lost 4 eq. hydrogen, and gained 4 eq. oxygen. But the best analyses of these resins agree even better with the formula $C_{40}H_{30}O_4$. If this last be the correct formula, $C_{40}H_{32}$ have lost 2 eq. of hydrogen, replaced by 2 eq. oxygen, yielding the oxide $C_{40}H_{30}O_2$; and this oxide has then combined with 2 eq. oxygen, giving the rational formula $C_{40}H_{30}O_2 + O_2$.

If from this we reason backwards to the constitution of oil of turpentine, it will appear that that oil is $C_{40}H_{30} + H_2$, or $C_{20}H_{15} + H$, in which formulæ part of the hydrogen belongs to the radical, and the remainder is removeable and replaceable by other elements, such as oxygen, iodine, or chlorine. This would also account for the tendency of oil of turpentine, as the hyduret of a compound radical, to unite with hydrochloric acid, the hyduret of a simple radical; just as ammonia, the hyduret of amide, or olefiant gas, the hyduret of acetylene, unite with the same acid.

From the balsams, which, as already mentioned, are mixtures of resins with essential oils, the former are obtained pure by distillation with water, as long as any oil passes over.

There are distinguished hard and soft resins. The hard resins are brittle, colourless when pure, although often tinged yellow or brown by foreign matters. They are heavier than water, and non-conductors of electricity. When warmed they have a slight odour, probably arising from traces of oil. Those which are insoluble in water are tasteless; many which are sparingly soluble have a bitter taste. They soften in boiling water, but generally require a higher temperature to melt them. They are decomposed by a strong heat, yielding combustible gases and volatile combustible liquids, with a residue of porous charcoal. They are easily inflamed, and burn with a smoky flame. When acted on by nitric acid the resins yield oxalic acid, and a series of products not yet examined.

The resins occurring in nature are generally mixtures of several, differing in their characters. Some are exceedingly soluble in cold alcohol, while others are dissolved with difficulty even by boiling alcohol. Several resins may be obtained in crystals from their alcoholic solutions; and the addition of water to all such solutions precipitates the resin, giving the mixture a milky aspect.

Many resins are soluble, others insoluble, in ether. They dissolve in fixed and essential oils, and also in sulphuret of carbon. The action of alkalis distinguishes one class of resins from another. A certain number, when dissolved, redden litmus, combine with bases, and possess all the characters of acids. Others are neutral, and do not combine with bases.

The most decidedly acid resins decompose the carbonated alkalis with the aid of heat, and readily dissolve in caustic alkalis. Their solution in alcohol is not precipitated by ammonia, and the precipitate caused by water is entirely soluble in ammonia. The alcoholic solution of the neutral resins is precipitated by ammonia.

The acid resins when dissolved in ammonia cause a crystalline pre-

precipitate in nitrate of silver, which is insoluble in excess of ammonia. The neutral resins cause no such precipitate.

The compounds of the acid resins with alkalies are called resinous soaps; but they cannot, like true soaps, be separated from their solutions by common salt, and when concentrated they do not form mucilaginous or gelatinous solutions, as soaps do. These solutions, however, froth when agitated, like a solution of soap. Some of these resinous soaps are insoluble in caustic potash, others soluble.

Common Resin, or *Rosin*, is obtained from the turpentine or balsam of *Pinus sylvestris*, *pinaster*, *abies*, and *picea*, by distillation with water till all the oil is removed. It is also named Colophon or Colophonium. It is nearly white when pure, (*Resina alba*,) but is commonly yellow or brown. It is a mixture of three acid resins, Sylvic, Pinic, and Colopholic acids.

Sylvic Acid is extracted from the resin by weak alcohol, and purified by stronger alcohol. It crystallizes in minute prisms, which lose no weight when heated to 212° . With alkalies it forms salts, which are soluble in ether and alcohol.

Formula, $C_{20}H_{15}O_2$ (Trommsdorff), or $C_{20}H_{16}O_2$ (Rose).

Pinic Acid is left undissolved by alcohol of 72 p. c. It is purified by combining it with oxide of copper, which is done by adding acetate of copper to its solution in strong alcohol. The pinate of copper is decomposed by hydrochloric acid, and the pinic acid repeatedly boiled with water. It does not crystallize, but in other respects is analogous to sylvic acid. Its formula is $C_{20}H_{15}O_2$. (Liebig.)

Colopholic Acid is produced by distilling pinic acid, and has a brown colour, but the same composition, and a stronger affinity for bases. When colophon has been strongly heated, part of the pinic acid is always converted into colopholic acid, so that it is present in that substance in variable quantity.

In the turpentine of *Pinus maritima* Laurent has discovered another acid, *Pimaric Acid*, which is isomeric with the preceding acids, and which crystallizes from hot alcohol. By distillation in vacuo it yields another isomeric modification, *Pyromaric Acid*; and, by the action of nitric acid, a third acid, *Azomaric Acid*, the formula of which is $C_{20}H_{11}NO_8$. When pimaric acid is distilled under the ordinary pressure, it yields a neutral substance, *Pimarone*, which contains 1 at. of water less.

Fremy, by distilling resin with lime, obtained two oils, Resinone and Resinéone; the former of which is $C_{10}H_9O$, the latter $C_{29}H_{23}O$.

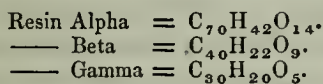
When common resin is repeatedly heated with water to dryness, it yields what is called pitch, shoemaker's rosin, or Burgundy pitch. A

still stronger heat produces the black pitch used for naval purposes. When distilled, resin yields a large quantity of gas of good quality for illumination.

The *Resin of Copaiva Balsam*, when purified from the essential oil, is a crystallizable acid resin, and has the same composition in 100 parts as Colophon or Camphor. According to Rose, its formula, deduced from its salts, is $C_{40}H_{32}O_4$.

The *Resin of Elemi* contains two, one of which is crystallizable, but both are neutral. Their composition is the same as that of the resins already described. The resin called Gum Animé, from *Hymenæa Courbaril*, likewise contains two resins, which seem to have acid properties. The resin of Euphorbium seems to be identical in composition and in most of its properties with that of Elemi.

Gum Benzoin, the inspissated juice of *Styrax Benzoin*, contains, besides benzoic acid and an essential oil, three resins, namely, resins alpha, beta, and gamma. The latter is acid, the two former neutral. According to Van der Vliet, their composition is as follows:—



It is obvious that resin alpha contains the elements of the other two; and in fact, if the original mixture be long enough boiled with carbonate of potash, the resin alpha disappears, while gamma is dissolved, and beta left.

Styracine.—The balsams of Mecca and Peru, and storax, contain resin, essential oil, and, in the two latter, benzoic and cinnamic acids. The resins have been little examined; but Simon has extracted from storax a crystalline substance, which he calls Styracine. It is neutral, and has the properties of a resin. Its formula is $C_{24}H_{11}O_2$. Distilled with nitric acid, it yields hydrate of benzoyle, hydrocyanic acid, and other products. When distilled with hydrate of lime, it yields an oil, isomeric with benzine, but differing from it in properties; and, when distilled with aqua potassæ, it yields another oil, *Styracone*, while the alkali is found combined with cinnamic acid, and mixed with a resinous matter. (Simon.)

Guaiacum, the resinous mass derived from *Guaiacum officinale*, contains a peculiar resin, distinguished by the property of striking a blue colour with many substances, such as mucilage of gum arabic, the roots of althæa, of cochlearia, of potato, of endive, of onions; also with nitrous acid, nitrous ether, and sweet spirit of nitre, as well as salts of iron and copper. The alcoholic tincture of guaiacum is the form in which this reaction is best observed. The guaiacum itself, by exposure to the

air, becomes blue or green. It contains, besides more than one resin, not sufficiently studied, a bitter acrid substance, *Guaiacine*, the nature of which is uncertain. Guaiacum is used in medicine in the form of tincture and in pills; and its compound with potash, called soap of guaiacum is also employed.

Lac is obtained from punctures made by an insect in several species of *Ficus*, and also from *Zicyphus jujuba*. It occurs in three forms: stick, seed, and shell lac; the latter being the purest. It contains several resins, along with a peculiar colouring matter. It is an ingredient in the better kinds of sealing-wax, and is much used for varnishes.

Mastic, from *Pistachia lentiscus*, and *Sandarac*, from *Juniperus communis*, grown in tropical regions, are two fragrant resins, containing each two or three different resins, and are also much used in making varnishes.

Copal, said formerly to have been derived from *Rhus copallanum*, seems by later accounts to be obtained from various species of *Hymenæa*, *Trachylobium*, and *Vouapa*. It has so much resemblance to amber, that it might be supposed to have a fossil origin; and, at all events, it has probably been long exposed to the action of the air before it has been collected. It is, of all resins, that which makes the finest varnishes; but it is at the same time the most difficult to dissolve. It may be dissolved in absolute alcohol, by first acting on it with aqua ammoniæ, which softens it into a gelatinous mass, and then adding the alcohol in small portions, with the aid of heat. It may likewise be dissolved in alcohol after being softened with ether. It is somewhat soluble in oil of rosemary, less so in oil of turpentine. But the common copal varnish is made by melting it cautiously, and adding oil of turpentine heated to a certain point. According to Unverdorben, copal contains not less than five different resins, with a trace of essential oil.

The resin called *Dammar*, lately introduced, is derived from some unknown tree. It resembles copal, and makes excellent varnish.

Other resins, of whose chemical characters little is known, are Dragon's blood, from *Dracena Draco*, Takamahaka, Ladanum, the resin of Jalap, the root of *Convolvulus Jalappa*, that of Scammony, from *C. scammonium*, that of castor, that of birch bark, &c.

The following plants likewise contain resinous substances:—*Iris florentina*, *Piper nigrum*, *Capsicum annuum*, *Pimpinella saxifraga*, *Helleborus hyemalis*, *Arnica montana*, *Anthemis pyrethrum*, &c.

RESINOUS VARNISHES.

These varnishes are made by dissolving resins in strong alcohol or oil of turpentine. The resins principally used for varnishes are mastic, sandarac, shell lac, elemi, and copal. To dissolve the latter, it is melted, mixed while hot with a little drying oil, and to the mixture oil of turpentine, in quantity equal to the resin, is added by small portions. Spirit varnishes are more brittle, those with oil of turpentine more plastic, as the oil itself in drying yields a soft resin.

PRODUCTS OF THE DISTILLATION OF COMMON RESIN.

When resin is subjected to heat in close vessels, it yields a large quantity of gaseous carbohydrogens, and several liquids, also composed of carbon and hydrogen. The subject has been investigated by Frémy, and by Pelletier and Walter.

Frémy states, that, when distilled at the lowest possible temperature, resin yields, besides water and other products, an oily liquid, *Resineine*, the formula of which is $C_{20}H_{15}O$.

When distilled at a higher temperature, there is obtained, according to Pelletier and Walter, a liquid, *Retinaphtha*, the formula of which is C_7H_4 . Treated with chlorine, retinaphtha yields a compound $C_{14}H_6Cl_2$; and a similar compound may be formed with bromine. Along with retinaphtha there is formed another liquid, less volatile, *Retinyle*, the formula of which is C_9H_6 ; and in the more fixed and oily product of the distillation of resin there are found a liquid, *Retinole*, the formula of which is C_8H_4 , and a solid compound, in appearance like a crystalline fat, which is called *Metanaphthaline* or *Retistérène*, and which has the composition of naphthaline.

NON-AZOTIZED VEGETABLE COLOURING MATTERS.

The varied colours of vegetables are owing to the presence of certain definite chemical compounds, which are called colouring matters. They are very numerous, and two or more are commonly found together. It is consequently difficult to obtain them in a state of purity, and hence their chemical characters are but imperfectly known.

Many of them are soluble in water; some only in alcohol or ether. They are all capable of combining with alkalies, and many of them combine also with acids. When exposed to light, especially if moist, they are bleached, absorbing oxygen at the same time; and their ten-

dency to absorb oxygen is much augmented when they are dissolved in alkaline fluids.

The colour of these substances is generally changed by the action both of acids and alkalies : the latter change the yellow to brown, the red to violet, blue, or green; while the former change the blue to red, and the red to a brighter tint.

Many of these colouring matters are not found in the living or fresh plant with the properties which they exhibit when separated by chemical means. Thus madder-root, when fresh, is yellow, and becomes red only after undergoing a species of fermentation; fresh logwood is brownish yellow, and becomes red by exposure to the air. In such cases, the colouring matter is formed by absorption of oxygen; and, when this is removed by deoxidizing agents, the colour is destroyed, but is often restored on exposure to the atmosphere.

Some colourless substances, such as gallic and tannic acids, when dissolved in an alkali, rapidly absorb oxygen, and give rise to dark blue or purple colouring matters.

Another class of colourless substances, which absorb oxygen when in contact with ammonia, give rise to very fine colouring matters. In this way are produced indigo, litmus, orceine, phloridzeine, &c. As these colouring matters, however, contain nitrogen, we shall describe them in a separate section.

All vegetable colouring matters are destroyed by chlorine, and cannot afterwards be restored. Most of them are bleached by sulphurous acid; but, on the addition of a stronger acid, the colour reappears, modified by the action of the acid employed.

The tendency of these colouring matters to combine with alumina is very powerful. They also combine readily with peroxide of tin, and with other similar oxides, which are, as it were, intermediate between acids and alkalies. The compounds thus formed are insoluble in water, and may be used in painting. They are called *lakes*.

Alumina, and the other oxides above alluded to, are also employed to attach the colouring matters to cloth, for the fibre of which these oxides have also a strong attraction.

The number of colouring matters is so great, and their chemical relations and composition are so little known, that we can only give a list of the more important.

1. YELLOW COLOURING MATTERS.

Turmeric yellow, or *Curcumine*, from the root of *Curcuma longa*.—It is extracted by alcohol, has a resinous aspect, and, when powdered,

a bright yellow colour. It is turned brown by alkalies, and is used as a test of alkalinity.

Gamboge yellow is extracted by ether from gamboge, the inspissated juice of *Garcinia Gambogia*, or *Stalagmites gambogioides*. It is resinous, and acts as a drastic purgative. It amounts to from 60 to 90 per cent. of gamboge.

Annotto is obtained by kneading with water the seeds of *Bixa orellana* or *Metella tinctoria*. According to Chevreul, it contains two colouring matters, a yellow and a red.

Carotine is the colouring matter of the carrot, *Daucus carota*. It is extracted by ether, and crystallizes in small ruby-red crystals, which are soluble in fixed oils.

Rhabarberine or *Rheine* is found along with tannin in the different varieties of rhubarb. It is soluble in alcohol, crystalline, and of an orange colour. It dissolves in alkalies with a violet colour; and from this solution alum throws down a fine red lake. It is fusible, and may be volatilized without decomposition.

Rhaponticine, analogous to the preceding, is found in *Rheum rhaponticum*.

Woad yellow, or *Luteoline*, is found in every part of woad, *Reseda luteola*. It is volatile and crystallizable.

Quercitron yellow, or *Quercitrine*, is the colouring matter of the bark of *Quercus nigra*, (*Q. tinctoria*, Mich.) According to Bolley, it is a yellow powder, partly crystalline, the formula of which is $C_{16}H_8O_9 + HO$. By adding to its solution in alcohol an alcoholic solution of acetate of lead, Bolley obtained a yellow salt, which he found to be $C_{16}H_8O_9.PbO$. He calls it *Quercitric acid*.

Morine, obtained by Chevreul from the wood of *Broussonettia* or *Morus tinctoria*. Yellow bitter needles, soluble in alcohol and ether. When distilled, it is partly decomposed, yielding a yellow liquid, which on cooling solidifies into reddish orange crystals. A similar substance is obtained from *Rhus cotinus*.

Safflower yellow is extracted by water from *Carthamus tinctorius*. It is not yet known in a state of purity.

Saffron yellow, or *Polychroite*, is the chief ingredient in the petals of *Crocus sativus* (saffron). It has not been produced in a state of purity.

Similar yellow colouring matters, often crystalline, are obtained from the flowers of *Datisca cannabina*, *Spiraea ulmaria*, *Narcissus pseudo-narcissus*; also from *Lichen parietinus*, from nut-galls, from *Chelidonium majus*, *Genista tinctoria*, *Serratula tinctoria*, *Betula alba*, *Rhamnus cathartica*, *R. infectoria*, and other plants.

Xanthophyll, or the *yellow of leaves*, is found in those leaves which become yellow in autumn. It is probably formed from *Chlorophyll*, the *green of leaves*, which, however, cannot be reproduced from it.

2. RED COLOURING MATTERS.

Dragon's blood, or, when pure, *Draconine*, is obtained from the gum-resin so called, which is produced by several species of *Calamus*, also by *Dracæna draco* and *Pterocarpus draco*. In mass it is reddish brown, in powder bright red. Dragon's blood is used in painting, dyeing, and varnishing.

Santaline is the red colouring matter extracted by alcohol from the wood of *Pterocarpus santalinus*. It has, like the preceding, a resinous aspect, and a dark red colour with frequent reflection of green. It is very soluble in alkalies; also in acetic acid, alcohol, and ether.

Anchusine, or *Anchusic Acid*, obtained from the root of *Anchusa tinctoria*. It yields a dark red fusible mass, which, if cautiously heated, yields violet-coloured vapours. It dissolves in alkalies with a blue colour, and is used as a test of alkalinity. It is properly the false alkanet. The true or oriental alkanet is obtained from *Lawsonia inermis*. (See Journal de Pharmacie, (1824,) page 405.)

A similar resinous red colouring matter is obtained from the flowers and seeds of *Hypericum perforatum*, and from the leaves of *Bignonia chica*.

Safflower red, or *Carthamine*.—It is extracted from *Carthamus tinctorius* (previously purified from the yellow matter by acetic acid) by a solution of carbonate of soda. When this is carefully neutralized by citric acid, carthamine is precipitated. It yields a dark red powder, reflecting a metallic green on the surface, but exhibiting a beautiful reddish purple in very thin layers. It has acid properties, and is used for dyeing rose-colour; also in painting, where it is often employed in the form of what are called pink saucers; and for rouge, under the name of *Rouge végétale*.

Madder.—This substance, the wood of the root of *Rubia tinctorum*, has been frequently examined. The latest experiments are those of Runge, who describes five colouring matters contained in it: three red, insoluble in water; one yellow, soluble in water; and one brown, which is insoluble.

The three red colouring matters are *madder purple*, *madder red*, and *madder orange*.

When the madder is washed with cold water, and boiled with a strong solution of alum, the filtered liquid on cooling deposits a red-

dish brown substance, chiefly composed of *madder red*. When purified from the purple, it forms a crystalline brownish yellow powder. It is fusible, and sublimes in brilliant orange needles. It gives to alcohol and ether a reddish yellow colour, to acids a yellow, to ammonia a purple, and to potash or lime a violet tint. It is the substance which produces the so-called Turkey red dye.

The solution which has deposited the mass containing the *madder red*, when acidulated with sulphuric acid, deposits slowly a red precipitate, which contains the greater part of the *madder purple*. It dissolves, when pure, in alcohol, and is deposited in orange crystals. It is volatile, but does not yield a crystalline sublimate. Alkalies dissolve it with a bright red colour.

To obtain the *madder orange*, the roots, previously well washed, are digested with tepid water, and the liquid strained through muslin. On standing, it deposits the *madder orange* in glimmering scales, which are purified by solution in alcohol, from which they are deposited on cooling. It dissolves in ammonia with a reddish brown colour, in potash with a rose-red. It may be sublimed, and yields a yellow mass.

These three colouring matters, together or separately, give all the different tints obtained from madder. The *Alizarine* of Robiquet (from alizari, the name given to madder in the Levant) is chiefly madder red; but, as it is obtained by sublimation, and as all three are volatile, it is necessarily mixed with the other two. They are all soluble in albumen, and have a tendency to combine with phosphate of lime. Hence, in animals fed with madder, the bones become red.

Madder yellow is obtained by acting on madder with water, and adding lime to the solution. The precipitate thus formed is dissolved in acetic acid, and the solution evaporated to dryness. Alcohol now dissolves the yellow matter, which is precipitated of a scarlet colour by acetate of lead. When this precipitate is decomposed by sulphuretted hydrogen, there is obtained a fine yellow solution of madder yellow.

Madder brown is insoluble in water or alcohol, soluble in alkalies. It cannot be used in dyeing.

It has been already mentioned that fresh madder-root is not red, but yellow; and that the red colour is formed by a species of fermentation, or rather decay, to which the oxygen of the atmosphere is essential. This change has not been properly studied; and it is not improbable that all the colouring matters of this dye stuff are products of the decomposition of one and the same original compound. They all yield, when carefully heated, a sublimate of orange crystals, called by Robiquet and Colin, who discovered them, *Alizarine*. These crystals may be made to yield all the tints of red obtained from madder; and, when

fixed on cloth, colours thus obtained are as durable as those made in the ordinary way from the root.

When cotton cloth is treated with acetate of alumina, a portion of the earth attaches itself to the fibre; and, when the cloth is now boiled with madder, the colouring matter combines with the alumina, and is thus fixed on the cloth in tints of red, varying with the amount of madder employed. If acetate of iron be used, the tints obtained are purple.

The process for obtaining the Turkey red is very complicated, and is not yet sufficiently understood to enable us to explain the effect produced by the different means employed. There is little doubt that it will be found to admit of much simplification, when the subject shall have been properly investigated; for it has already been ascertained that the sheep's dung, used in the process, acts by the phosphates it contains, and may be replaced by those phosphates when prepared in an appropriate form.

Alizarine.—To obtain this substance, madder red, however prepared, may be gently sublimed: or powdered madder may be cautiously charred by adding it gradually to its own weight of oil of vitriol, which decomposes everything except the alizarine. (Robiquet and Colin.) The carbonaceous mass is well washed with water, dried and gently heated, when it yields crystals of alizarine. These crystals have a fine orange-red colour. They dissolve sparingly in hot water and alcohol, to which they give a rose-red colour. They also dissolve in alkalies with a purple colour. Alizarine appears to stand in the same relation to the red of madder as sublimed indigo to common indigo. It has not yet been obtained in a state of perfect purity, so that its composition is not ascertained.

Madder lake, much prized as a pigment, is made by washing madder with cold water, boiling the residue with a solution of one part of alum in twelve of water, and precipitating the decoction gradually with carbonate of soda, or with borax. The precipitates first obtained are the most beautiful.

Hæmatoxylin.—This is the red colouring matter of logwood, *Hæmatoxyllum campechianum*. It is soluble in water, more so in alcohol, from which latter solvent it crystallizes in shining orange crystals. It colours water red; acids brighten the colour, alkalies turn it to purple or blue. It is decolorized by sulphuretted hydrogen and other deoxidizing agents, but becomes red again by exposure to the air.

With an alum mordant, logwood yields a violet dye; with iron, a black. It is used in dyeing black cloth and hats, which are hence reddened by acids.

Braziline is the red of Brazil wood (*Cæsalpina braziliensis*, *C. crista*?) Soluble in water and alcohol; and crystallizable, according to Chevreul, who obtained small orange-coloured needles. Acids turn it yellow, alkalies violet. In the wood it is yellow, owing to the presence of acid, and the addition of alkalies developes the colour. It is a delicate test of alkalinity. With alum it yields a red dye, which is brilliant, but not durable.

A still finer but equally fugitive dye is obtained from *camwood*, a wood imported into England from Africa, the origin of which is unknown.

The red colouring matter of many flowers, such as *Rosa centifolia*, *Pæonia officinalis*, *Papaver rhæas*, *Althæa rosea*, *Dianthus caryophyllus*, *Cactus*, *Gladiolus*, and many more, is best extracted by weak alcohol. It is obtained as a dark red mass, yielding a bright red powder, soluble in water and weak alcohol. It is turned blue or green by alkalies, and is very fugitive. It is not known in a state of purity.

Another variety of red colouring matter is found in autumn in the leaves and fruit of certain plants. It has been called *Erythrophyll*; but its properties are little known.

3. BLUE COLOURING MATTERS.

These are found chiefly in flowers; also in some fruits and leaves. They are analogous to the red colouring matters of flowers, many, perhaps all, of which are naturally blue, but reddened by acids. They are turned green by alkalies; and many, such as the blue of *Viola odorata*, are used as tests of alkalinity. In some plants, such as *Crozophora tinctoria*, *Mercurialis annua*, *M. perennis*, &c., the juice, at first green, becomes blue on exposure to the air. In the first-mentioned plant, this change is hastened by exposure to ammoniacal vapours; and hence the resulting blue is probably azotized, as is the case with indigo. Unlike indigo, however, the blue of *Crozophora tinctoria* is reddened by acids.

The blue of the over-ripe fruit of *Rhamnus catharticus* is distinguished from the preceding by the action of alum, which, as well as alkalies, changes it to green.

4. GREEN COLOURING MATTERS.

Chlorophyll.—This is the most abundant of all vegetable colouring matters, being found in the leaves, stalks, unripe fruit, and juice of all

except the very lowest classes of plants, such as algæ, mosses, and sponges. It has been studied most recently by Berzelius.

It is extracted by ether, and purified by the successive action of alcohol and hydrochloric acid, from which last solvent it is precipitated by water. It forms a dark green mass, the powder of which is grass-green. Alcohol is its best solvent, but dissolves it sparingly. It is soluble in acids and alkalies, both of which it colours green. It is decolorized by chlorine. Berzelius has described two modifications of it, besides that above mentioned. It possesses few marked properties, although it has a tendency to combine with alkalies, such as lime, baryta, and oxide of lead. Its composition is unknown, as it has probably not been obtained in a state of purity. It may be considered as intermediate between fat or wax and the resins.

Polychrome.—This substance, in some respects analogous to the colouring matters, is found in several plants, as, for example, in the bark of the horsechestnut and in quassia wood. It is dissolved by water, precipitated by acetate of lead, the precipitate decomposed by sulphuretted hydrogen, and the filtered liquid evaporated to the consistence of syrup. After some time the polychrome crystallizes. It is purified by repeated solution in a mixture of alcohol and ether. It is sparingly soluble in cold, readily in hot water. The latter solution gelatinizes on cooling. A solution of polychrome appears colourless by transmitted light, but blue by reflected light; and exhibits a curious play of colours, visible when 1 part of polychrome is dissolved in 1,500,000 of water. Acids destroy this play of colours, alkalies increase it. According to Trommsdorff, jun., its formula is $C_{16}H_9O_{10}$, or $C_{16}H_8O_9, HO$.

NON-AZOTIZED VEGETABLE PRINCIPLES, THE TRUE NATURE OF WHICH IS NOT EXACTLY ASCERTAINED.

In the earlier works on Vegetable Chemistry, a number of substances were described under the general names of *Extractive principle* and *Bitter principle*. Later researches have shewn that what was called extractive principle is the result of the decomposition, probably of several substances, during the operations to which the vegetable was subjected; and that very many plants contain peculiar, often crystallizable compounds, having a bitter taste, and which are often, doubtless, the active principles of the vegetable in which they occur.

Few of these have been sufficiently examined; and the whole sub-

ject of these bitter non-azotized compounds, and of the changes they undergo, requires a thorough investigation, which would certainly throw much light on organic chemistry. The researches on Salicine and Phloridzine, compounds formerly described, and belonging to this class, have led to most important results, and have enabled us to classify these compounds; but our knowledge of the compounds now to be mentioned is too limited to enable us to adopt any system of classification, and we are compelled to confine ourselves to a brief descriptive catalogue of the more important among them.

Gentianine.—Extracted by ether from the root of *Gentiana lutea*, and purified by solution in alcohol. It forms golden yellow crystals, of a very bitter taste, which may be sublimed. According to Trommsdorff, when quite pure, it is no longer bitter, and has acid properties, expelling carbonic acid from the alkaline carbonates, and forming with the alkalis golden yellow crystallizable salts.

Absinthiine, from the flowers of wormwood, *Artemisia absinthium*. It is white and partly crystalline, intensely bitter, very soluble in alcohol. It may be combined with metallic oxides by double decomposition.

Santonine is found in the flowers of several species of *Artemisia*, and in the so-called *Semen Cynæ*, which is much used as a vermifuge, and is a mixture of the flowers, buds, and unripe seeds of these plants.

Four parts of this mixture are digested with one-half of slaked lime and 20 of alcohol at 90 per cent. The santonine is dissolved, in combination with lime and with a brown resin. It is separated by acetic acid, but is still contaminated with resin. This is removed by washing with a little alcohol; and the residue being dissolved in 8 or 10 parts of alcohol at 80 p. c. and boiled with animal charcoal, the liquid, on cooling, deposits santonine in colourless crystals, which must be kept in the dark, as they become yellow when exposed to light. It is tasteless and inodorous, fusible and volatilizable, sparingly soluble in water, more easily in alcohol and ether. It has acid properties, and forms salts with potash and soda, the latter of which crystallizes. Acids dissolve it without altering it, and water precipitates from the solution the santonine unchanged. It forms crystalline salts with lime and baryta, and insoluble compounds with many metallic oxides. Its composition is represented by the formula C_5H_3O (Ettling); but its atomic weight must be twelve times greater, to judge from its capacity of saturation.

Populine is found in the bark and leaves of *Populus tremula* along with salicine. It forms delicate white needles, which have a sweet

taste like that of liquorice. It is sparingly soluble in water, readily in alcohol, and is reddened by oil of vitriol. (Braconnot; De Koninck.)

Liriodendrine is found in the bark of the root of *Liriodendron tulipifera*. (Emmet.) It forms white crystals, like those of boracic acid; sparingly soluble in water, more soluble in alcohol, with a bitter and balsamic taste.

Picrolichenine.—Discovered by Alms in the lichen *Variolaria amara*, from which it is extracted by alcohol. It is purified from a green matter which accompanies it by washing with a dilute solution of carbonate of potash. It forms obtuse double four-sided pyramids, which have a most intense bitter taste. When acted on by ammonia in a close vessel, it dissolves; and after some time the solution becomes yellow and deposits yellow crystals, which are not bitter. When the ammoniacal solution is exposed to the air, a dark red substance is formed, which indicates an analogy between this substance and erythric acid, which, as will be hereafter mentioned, occurs in other lichens. Its composition is unknown, but it contains no nitrogen. It is said to be powerfully febrifuge.

Cetrarine is analogous to the preceding. It occurs in several lichens, as in Iceland moss; (*Cetraria islandica*,) and in *Sticta pulmonacea*. It is extracted by alcohol. It forms a fine white powder, very bitter to the taste. Concentrated hydrochloric acid colours it deep blue. Its other properties are little known, but it is said to be used as a febrifuge in Italy.

Elaterine is the active principle of elaterium, the inspissated juice of the fruit of *Momordica elaterium*. The elaterium is dissolved in hot alcohol, and the concentrated solution thrown into water, which precipitates the elaterine. By repeating this process, it is obtained pure. (Morries.) It forms delicate silky crystals of a very bitter taste. One-sixteenth of a grain acts as a drastic purgative. Its composition, according to Zwenger, is $C_{20}H_{14}O_5$. It merits a more minute examination.

Colocynthine.—The bitter and purgative principle of colocynth, which is the pulp surrounding the seeds of *Cucumis colocynthis*. It is obtained by evaporating the infusion made with cold water, at first in oily drops, which afterwards solidify into a brown brittle mass. It is soluble in water, alcohol, and ether, intensely bitter, and acts as a drastic purgative. Its chemical characters are imperfectly known, and it is probably a mixture.

Bryonine.—Obtained by a somewhat similar process from the juice of the root of *Bryonia alba* and *B. dioica*. It forms a brown or yel-

lowish white mass, having a taste at first sweetish, then acrid and very bitter; soluble in water and alcohol, insoluble in ether. It appears to contain nitrogen, and is probably a mixture of several compounds. It is a drastic purgative, and has poisonous properties.

Mudarine is found in the bark of the root of *Calotropis Mudarii*. (Duncan.) It is soluble in water and alcohol. The aqueous solution gelatinizes when heated to 95°; at a higher temperature it is coagulated, the mudarine separating as a viscid mass. On cooling, it is slowly but completely redissolved. Mudarine has powerful emetic properties.

Scillitine.—Obtained from the juice of squills, the bulb of *Scilla maritima*. A brittle mass, of a nauseous bitter taste. It acts as an emetic and as a purgative, and appears to be poisonous. (Tilloy.)

Cathartine.—Similar to the preceding. Obtained from the leaves of *Cassia Senna* and *C. lanceolata*, and from some other plants. It has a bitter nauseous taste, and purgative properties.

Antiarine.—Formula $C_{14}H_{10}O_5$. (Mulder.) Is the active principle of the upas poison, or *Upas antiar*, which is a gum-resin derived from *Antiaris toxicaria*, a tree found in Borneo, Sumatra, and Java. The upas contains 3.56 per cent. of antiarine. It forms small scaly crystals, soluble in 250 parts of cold water, 70 of alcohol, and 2790 of ether. It dissolves in 27.4 parts of hot water. It has neither acid nor alkaline properties. It is a frightful poison, and infallibly causes death, even when introduced into a wound in small quantity; the fatal event being preceded by vomiting, diarrhœa, and convulsions. No antidote is known.

Xanthopierine is found in the bark of *Xanthoxylum Clava Herculis*. It forms greenish yellow silky crystals, intensely bitter and astringent. It is very soluble in alcohol, and has neither an acid nor an alkaline reaction. Its action on the system has not been studied, but the bark is used as a remedy in the Antilles.

Columbine.—Obtained from Columbo, the root of *Menispermum palmatum*. It is extracted by alcohol or ether. Forms colourless and transparent oblique rhombic prisms, or delicate white needles: is neutral, fusible, and contains no nitrogen. It is very bitter, and becomes still more so when dissolved in acetic acid. It is the active principle of columbo. (Wittstock.)

Quassine is the bitter principle of the wood of *Quassia amara*. When pure, it forms small white opaque prisms, which are intensely bitter, and very soluble in alcohol. From the analysis of Wiggers, its formula is probably $C_{20}H_{12}O_6$.

Lupuline is the bitter principle of hops, the female flowers of *Hu-*

mulus lupulus. It is neutral, uncrystallizable, soluble in water and alcohol, and very bitter.

Lactucone is a substance found in *Lactucarium*, the inspissated juice of *Lactuca sativa*, *L. virosa*, and *L. scariola*. It forms fine colourless needle-shaped crystals, tasteless, inodorous, and without action on the system. Its composition is $C_{40}H_{32}O_3$. (Lenoir.) It is sparingly soluble in water, very soluble in alcohol. The anodyne effects of lactucarium are most probably to be ascribed to another compound, probably basic, not yet insulated.

Ergotine.—Discovered by Wiggers in the ergot of rye, *Secale cornutum*. It is obtained as a brown powder, of a pungent and bitter taste, and is conceived by Wiggers to be the active principle. He describes it as narcotic and poisonous; but its composition and properties are unknown, and it is most probably a mixture.

Porphyroxine.—Discovered by Merck in Bengal opium. It forms small brilliant crystals, which, when dissolved in diluted mineral acids and heated, yield a red colour. It is neutral, soluble in alcohol and ether, insoluble in water. It is quite distinct from the other crystalline substances found in opium, but as yet has been little examined.

Saponine is found in the root of *Saponaria officinalis* and *Gypsophila Struthium*. It is extracted by alcohol, and purified by repeated crystallization from that solvent. It forms a white brittle mass, not crystallized. It has a taste at first sweetish, then acrid and irritating, and the smallest quantity of the powder introduced into the nostril causes violent sneezing. It is soluble in water; and the solution, even when very dilute, froths like a solution of soap. The root is used as a detergent.

Saponic Acid is produced by the action of acids and alkalies on saponine. It appears as a white powder, sparingly soluble in water, soluble in alcohol, and has very feeble acid properties. Its formula is $C_{26}H_{23}O_{12}$. (Frémy.)

Smilacine. *Syn. Parilline, Salseparine*.—Extracted by alcohol from *Sarsaparilla* (*Smilax sarsaparilla*). It is crystallizable, soluble in hot water and alcohol, colourless, and tasteless. Its solutions have the property of frothing. Its formula appears to be $C_{15}H_{13}O_5$. (Poggiale; Thubœuf; Petersen.) The Chinova bitter of Winkler, found in *China nova*, has been shewn by Büchner, jun., to be identical in its properties with smilacine; and Petersen has shewn that its formula is $C_{15}H_{12}O_4$, differing from that of smilacine only by 1 eq. of water.

Senegine. *Syn. Polygaline, Polygalic Acid*.—Is found in *Polygala senega* and *P. virginica*. It is a white powder, at first tasteless, after-

wards very acrid, and causing a feeling of astringency in the gullet. It also acts as a sternutatory. According to Quevenne its formula is $C_{11}H_{18}O_{11}$.

Guaiacine.—Discovered by Trommsdorff in the wood and bark of *Guaiacum officinale*. It forms a yellow brittle mass, which has a sharp acrid taste. It is no doubt one of the active principles of the gum-resin of guaiacum, and is the cause of its acrid taste.

Plumbagine occurs in the root of *Plumbago europæa*. It is extracted by ether, and forms fine orange-yellow crystals, which at first have a sweet taste, followed by a burning acrid sensation. It is neutral, and soluble in hot water. Alkalies give to its solution a cherry-red colour, but acids restore the yellow. The root also contains a peculiar fat, not yet investigated, which gives to the skin a lead-grey colour, whence the name of the plant is derived.

Cyclamine. *Syn. Arthanitine*.—Found in the root of *Cyclamen europæum*. It crystallizes in fine white needles, of a burning acrid taste, and having emetic and purgative properties.

Peucedanine.—Discovered by Schlatter in the root of *Peucedanum officinale*. Extracted by alcohol. It forms delicate white prisms, fusible, insoluble in water, soluble in alcohol and ether. The solution has an acrid burning taste. It is neutral. Formula, C_4H_2O . In some roots that had been long kept Erdmann found a modification of peucedanine, differing from it only in being insoluble in ether. Its formula was $C_8H_4O_3$; which only contains 1 at. of oxygen more than the formula of peucedanine doubled, and was, therefore, probably formed from it by the action of the atmosphere.

Imperatorine.—Found by Osann in the root of *Imperatoria Ostruthium*. Is extracted by ether. It forms long transparent prisms, has an acrid burning taste, is neutral, fusible, insoluble in water, soluble in alcohol and ether. Formula, $C_{24}H_{12}O_5$. (F. Doebereiner.)

Phillyrine occurs in the bark of *Phillyrea media* and *latifolia*. It forms silvery scales, at first tasteless, afterwards bitter.

Fraxinine.—Found in the bark of *Fraxinus excelsior*. Fine six-sided prisms, soluble in water and alcohol. It has a bitter taste, and is neutral.

Tanghinine.—Extracted by ether from the seeds of *Tanghinia madagascariensis* after the fixed oil has been removed by pressure. It is crystallizable; soluble in water, alcohol, and ether; very bitter and acrid. It is also poisonous. (Henry and Ollivier.)

Melampyrine.—Found by Hünefeldt in *Melampyrum nemorosum*. It forms white prismatic crystals, devoid of taste and smell, and perfectly neutral.

Meconine.—Discovered by Couerbe in opium. It is dissolved, along with most of the other ingredients of opium, when water is used as the solvent; and, being soluble in water, it remains dissolved when morphia, narcotinc, &c. are precipitated by ammonia. Part of it, however, falls along with the precipitate. It is purified by the alternate action of alcohol, water, and ether; in all of which it is soluble with the aid of heat. When pure, it forms fine white prisms, which are at first tasteless, afterwards acrid. It is fusible, and may be sublimed unchanged. It requires for solution 266 parts of cold water, and 18 parts of boiling water. When heated with water it first melts into an oily fluid, and gradually dissolves. Sulphuric acid, diluted with half its weight of water, dissolves meconine, forming a colourless solution, which when heated becomes dark green. Water throws down from the green solution brown flocks, which dissolve in alcohol with a rose-red colour. From this alcoholic solution the salts of alumina, lead, and tin throw down fine red lakes. Meconine is quite neutral. Its formula, according to Couerbe, is $C_{10}H_5O_4$, or rather the half of this; but its composition cannot be considered as ascertained. By the action of chlorine it is converted into mechloic acid, and nitric acid changes it into nitro-meconic acid.

Mechloic Acid is formed, along with a resinous matter, when chlorine gas is made to act on fused meconine. When pure, it forms colourless crystals, strongly acid, which contain no chlorine. Its formula, according to Couerbe, is $C_{14}H_7O_{10}$.

Nitro-meconic Acid is formed by the action of strong nitric acid, aided by a gentle heat, on meconine. It crystallizes from its solution in hot water in regular yellow crystals. These are soluble in strong acids without change; but the addition of water destroys the yellow colour, and the acid is then deposited in colourless crystals. Alkalies dissolve it with a strong reddish yellow colour. According to Couerbe, its formula is $C_{20}H_9NO_{12} = C_{20}H_9O_7 + NO_5$ or $C_{20}H_9O_9 + NO_3$.

Cubebine.—Found by Soubeiran and Capitaine in Cubebs pepper (the seeds of *Piper Cubeba*). It is neutral, crystallizable, tasteless, sparingly soluble in water and alcohol. Its formula is probably $C_{34}H_{17}O_{10}$.

Olivile.—Found by Pelletier in the gum-resin of *Olea europæa*. It forms white needles, which have an acrid, sweet, and bitter taste. It is fusible, soluble in hot water and alcohol, insoluble in ether. It is neutral. Formula, $C_{12}H_9O_4$. (Pelletier.)

Olivine is the name given by Landerer to a bitter substance obtained by him in the form of white crystals from the leaves of *Olea europæa*. It is soluble in acids, but does not form crystallizable salts with them.

Amanitine is the poisonous principle of certain mushrooms, such as *Agaricus muscarius*, *A. bulbosus*, and others. It is not known in a pure state, and has only been obtained as a brown mass, the chemical properties of which are very imperfectly known.

The following substances are neutral, have generally a bitter taste, or are tasteless, and are to a certain extent problematical, as the observations regarding them are very imperfect. It is probable that many of them will be found identical with some of the preceding.

Alcornine, from Alcornoco, the root of *Hedwigia vergelioides*.

Alismine, from *Alisma plantago*.

Arnicine, from *Arnica montana*.

Asclepine, from the root of *Asclepias gigantea*.

Buenine, from the bark of *Buena hexandra*.

Canelline, from the bark of *Canella alba*.

Cascarilline, from the bark of *Croton eleutheria*.

Cassine, from *Cassia fistula*.

Centaurine, from *Erythræa centaurium*.

Colletine, from *Colletia spinosa*.

Coriarine, from *Coriaria myrtifolia*.

Cornine, from the bark of the root of *Cornus florida*.

Corticine, from the bark of *Populus tremula*.

Cytisine, from the seeds of *Cytisus laburnum*.

Daphnine, from the bark of *Daphne mezereum* and other species.

It is crystallizable.

Datiscine, from *Datisca cannabina*.

Diosmine, from the leaves of *Diosma crenata*.

Euonymine, from the seeds of *Euonymus europæus*.

Fagine, from *Fagus sylvatica*.

Geraniine, from the *Geraniaceæ*.

Granatine, from unripe Pomegranates.

Guacine, from Guaco leaves.

Hesperidine, from the spongy part of the Orange rind. Crystallizes.

Hyssopine, from *Hyssopus officinalis*.

Ilicine, from *Ilex aquifolium*. Crystallizable.

Lapathine, from *Rumex obtusifolius*.

Ligustrine, from the bark of *Ligustrum vulgare*.

Liliacine, from *Syringa* or Lilac.

Menyanthine, from *Menyanthes trifoliata*.

Narcitine, from *Narcissus pseudo-narcissus*.

Primuline, from the root of *Primula veris*.

Pyrethrine, from the root of *Anthemis pyrethrum*.

Rhamnine, from *Rhamnus frangula*.

Scordine, from *Teucrium scordium*.

Scutellarine, from *Scutellaria lateriflora*.

Serpentine, from *Aristolochia serpentaria*.

Spartiine, from *Spartium monospermum*.

Spigeline, from the root and leaves of *Spigelia anthelmia*.

Tanacetine, from *Tanacetum vulgare*.

Taraxacine, from *Leontodon taraxacum*.

Tremelline, from *Tremella mesenterica*.

Zedoarine, from the root of *Curcuma aromatica*.

LECANORINE.—ORCINE.—ERYTHRINE.

We shall here describe, in a separate section, a remarkable class of vegetable products, which are colourless, and contain no nitrogen, but, on exposure to the air in contact with ammonia, yield beautiful colouring matters, in which nitrogen is an essential element.

To this class of colouring matters belong those of Archil and Litmus; and the study of them forms a very proper introduction to that of Indigo, and, through Indigo, to the study of the azotized principles of the vegetable kingdom.

The lichens used in dyeing, and other allied species, have been shewn, by the recent researches of Schunck, of Rochleder and Heldt, and of Knop, to contain a peculiar class of compounds, possessing weak acid properties, which are in themselves colourless, but which, in contact with air and ammonia, give rise to dark-coloured compounds, some of which exhibit only various tints of brown, while others are blue, purple, or red, and form the foundation of the dye-stuffs procured from lichens, such as archil, cudbear, and litmus.

Lecanoric Acid. *Syn. Lecanorine.*—This acid was discovered by Schunck in *Variolaria lactea*, *Lecanora tartarea*, *Lecanora parella*, *Urceolaria scruposa*, and some other lichens. Rochleder and Heldt found it in *Evernia prunastri*. Schunck obtained it by acting on the lichens with ether, which dissolves at the same time another acid, *Parallellic Acid*, and a peculiar fat, coloured green by chlorophyll. The lecanoric acid was purified by solution in hot alcohol, and crystallization. Rochleder and Heldt extracted it by a mixture of ammonia and alcohol, to which one-third of its volume of water was then added, and the ammonia neutralized by acetic acid. The lecanoric acid is precipitated, and is purified by means of alcohol. It is white, composed of minute crystals, almost insoluble in water, sparingly soluble in cold alcohol and in ether. It is a weak acid, and dissolves in barytic water

and lime water, yielding solutions which coagulate on the addition of alcohol or of acids. When heated with baryta it is decomposed, yielding carbonate of baryta, and orcine which remains in solution. When exposed to heat it yields a sublimate of pure orcine, while carbonic acid is given off. When boiled with alcohol it is gradually but entirely converted into lecanorate of oxide of ethyle (pseudo-erythrine of Heeren), which dissolves in boiling water without residue. The formula of the crystallized acid is $C_{18}H_9O_9 = C_{18}H_8O_8, HO$. That of the acid, after long exposure to a heat of 212° , is $C_{18}H_8O_8$.

By the long-continued action of air and ammonia it is changed into a compound of a fine rich blue or purple colour. It is here first changed into orcine, from which there is formed, by the action of ammonia, a deep purple compound, *orceine*.

Lecanorate of Oxide of Ethyle. Syn. Pseudo-erythrine of Heeren; Erythrine of Kane.—When lichens containing lecanoric acid are exhausted by boiling with alcohol, this substance is obtained. It crystallizes with facility from its solution in hot water, and was taken for a natural constituent of the lichens, till Schunck ascertained its true nature. Its solution in water when long boiled is decomposed, and the substance disappears, being converted into orcine. When heated, it volatilizes unchanged; but, when boiled with alkalis, alcohol is given off, and the lecanoric acid is converted into orcine and carbonic acid. Formula, $C_{22}H_{13}O_9 = C_{18}H_8O_8 + C_4H_5O$.

Lecanorate of Oxide of Methyle is analogous to the preceding compound.

Parellic Acid.—This acid is extracted in part along with the former from the lichens by ether, and in part remains after the action of the ether, and is then extracted by hot alcohol. It is separated from lecanoric acid by means of baryta, with which it forms an insoluble salt. This is decomposed by hydrochloric acid, the precipitate of parellic acid is well washed, and purified by solution in hot alcohol. It forms either minute crystals, resembling those of lecanoric acid, or, by spontaneous evaporation, large transparent crystals, of great density. The formula of the former is $C_{21}H_8O_{10}$; that of the latter, $C_{21}H_9O_{11}$. The acid, after exposure to a heat of 212° , is $C_{21}H_7O_9$.

With ammonia parellic acid slowly becomes yellow, then brown. Heated with strong alkalis, it is decomposed, yielding carbonic acid, and other products not yet studied, one of which forms brilliant octohedral crystals.

There is also found in the above lichens, besides the fatty matters, an astringent compound, analogous to tannine.

Orcine.—This substance was discovered by Robiquet, who found it

in the *Variolaria orcina*, and considered it as pre-existent in that lichen. It has been shewn above to be a product of the decomposition of lecanoric acid, and we shall see that it is also formed from other substances.

Orcine forms large regular four-sided prisms, soluble in water and alcohol. The aqueous solution has a sweet taste. The crystals are fusible at 212° , and may be sublimed into a liquid, which, in contact with water, is reconverted into crystals of orcine.

Orceine.—Orcine dissolves in the fixed alkalies, and the solution becomes brown on exposure to the air. But, when dissolved in ammonia, it gradually acquires a deep blood-red colour, and there is formed a compound of ammonia with a new substance, *orceine*, which contains nitrogen as an essential element, besides that of the ammonia. On the addition of acetic acid orceine is precipitated as a brownish-red powder.

Orceine is soluble in ammonia with a blood-red colour, in fixed alkalies with a violet-red tint, and is precipitated unchanged by acids. With the salts of lead and silver the ammoniacal solution gives deep red precipitates.

Robiquet has shewn, that, during the conversion of orcine into orceine, oxygen is absorbed, and orceine is the only product, except water.

It is obvious that the composition of orcine must be closely related to that of lecanoric acid, from the fact that the latter is decomposed into the former, with the formation of carbonic acid. The analyses of orcine by Dumas, Will, and Schunck admit of two formulæ for that substance in its crystallized state. These are, $C_{16}H_{11}O_7$ and $C_{18}H_{12}O_8$.

According to Schunck, 1 atom lecanoric acid = $C_{18}H_8O_8$ is resolved into 2 atoms carbonic acid = C_2O_4 and 1 atom *anhydrous* orcine = $C_{16}H_8O_4$; to this are added 3 atoms water = H_3O_3 to produce 1 atom crystallized orcine = $C_{16}H_{11}O_7$.

This enables us easily to explain the formation of orceine, the formula of which, according to the analysis of Dumas, is $C_{16}H_9NO_7$; for 1 atom crystallized orcine = $C_{16}H_{11}O_7$, with the addition of 1 eq. ammonia NH_3 , and 5 eq. oxygen = $C_{16}H_{14}NO_{12}$; and if from this sum 5 atoms water = H_5O_5 be removed, there remains 1 atom orceine = $C_{16}H_9NO_7$.

According to Robiquet, the *Variolaria dealbata*, when boiled with alcohol, yields a decoction in which orcine is contained; but it deposits on cooling crystals of another substance, which has not been further examined.

When the alcoholic solution of this lichen is evaporated to dryness, and the orcine removed from the extract by hot water, ether extracts from the residue another crystalline substance, which Robiquet calls Variolarine. It is fusible, and may be sublimed without much change.

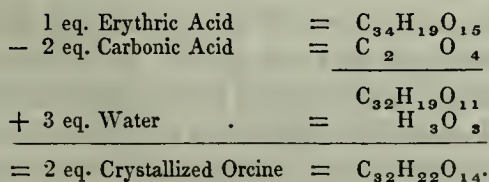
Both these substances resemble those described by Schunck; but our knowledge of all of them is too limited to allow us to pronounce them identical, although their identity is highly probable.

Erythric Acid. Syn. Erythrine (Heeren); Erythryline (Kane).—This acid is found in the *Rocella tinctoria*, a lichen which yields the best archil. It is extracted by boiling water, and purified by solution in alcohol. (Schunck.) The mother-liquid contains a bitter substance, which Schunck calls Picro-erythrine, and an astringent matter. Rocellic acid, which is a species of fatty acid, is also found in this lichen.

Erythric acid is the most important of all the substances found in the lichens, and is perhaps the only source of the colouring matters derived from them, so far as these are used in dyeing. It is, however, impossible to extract much of it from the lichen, because its solutions are decomposed by boiling. From 1 lb. of lichen Schunck obtained only about 50 grains of the acid.

It is soluble in alcohol, ether, and water, of which last it requires 240 parts at 212° to dissolve it. It crystallizes from alcohol in radiated groups. It would appear that Heeren's erythrine and Kane's erythryline are not quite identical with it, and that they are either products of its decomposition, or mixed with such products. By long boiling with water it is changed into picro-erythrine. When heated it yields a sublimate of orcine. It dissolves in alkalies, and in these solutions acids cause a gelatinous precipitate of erythric acid. When boiled with alkalies it is resolved, like lecanoric acid, into carbonic acid and orcine. The solution of erythric acid in ammonia, when exposed to the air, soon becomes dark purple. The analysis of the acid by Schunck gave the formula $C_{34}H_{19}O_{15}$; and that of its compound with oxide of lead, according to the same chemist, gave the formula $C_{34}H_{15}O_{11} + 4PbO$.

The conversion of erythric acid into orcine may be thus explained:—



When boiled with alcohol, erythric acid yields a crystalline compound, which was called by Heeren Pseudo-erythrine, but which Schunck has recently shewn to be identical with lecanorate of oxide of ethyle. It would appear, therefore, that erythric acid, when boiled with alcohol, is resolved into lecanoric acid, which combines with oxide of ethyle, and another compound. According to Schunck, this other compound is orcine; and, if from 1 eq. of erythric acid = $C_{34}H_{19}O_{15}$ we subtract 1 eq. orcine = $C_{16}H_{11}O_7$

there is left 1 eq. lecanoric acid = $C_{18}H_8O_8$.

Erythric acid is, therefore, probably a coupled acid, composed of orcine and lecanoric acid, and might be called *Orcinolecanoric Acid*. This accounts for the presence of 4 eq. of oxide of lead in the lead compound, for orcine combines with 3 eqs., and lecanoric acid with 1 eq. of oxide of lead.

Picro-erythrine. Syn. *Erythrine Bitter* (Heeren); *Amarythrine* (Kane).—This substance is formed from erythric acid when its aqueous solution is boiled. It is the cause of the bitter taste of the decoction of lichens containing erythric acid. It is sparingly soluble in cold water, more so in boiling water, soluble in alcohol and ether. When heated it yields a sublimate of orcine; and when boiled with baryta it yields orcine and carbonate of baryta. Its formula is $C_{34}H_{24}O_{20}$, so that in forming it erythric acid takes up 5 eq. of water.

Most of the substances above mentioned, namely, lecanoric acid, lecanorate of oxide of ethyle, erythric acid, orcine, and picro-erythrine, give with perchloride of iron a deep purple colour, and reduce the salts of silver and gold when boiled with them, ammonia being sometimes required in the case of the salts of silver.

Usnic Acid.—In the *Lichen rangiferinus* Rochleder and Heldt found a substance of the formula $C_{38}H_{17}O_{14}$, which is equal to 2 eq. lecanoric acid, minus 2 of oxygen, and plus 2 of carbon and 2 of hydrogen, or C_2H_2 . The same substance was found by them in *Usnea barbata* and *Ramalina calicaris*. This substance was also discovered by Knop in *Usnea florida*, also in *U. hirta* and *U. plicata*, and by him named *Usnic Acid*. It occurs in many lichens, such as *Parmelia hæmatomma*, *Biatora lucida*, *Lecidea geographica*, *Parmelia sarmentosa*, *Alectoria sarmentosa*, *Evernia sarmentosa*, *Cladonia rangiferina*, *C. uncinata*, and, indeed, all the numerous species of *Cladonia*, especially those which exhibit a red colour. It is extracted by ether, and purified by adding a little alcohol to the concentrated ethereal solution, when it is deposited in crystals of a sulphur-yellow colour, insoluble in water and alcohol. Like the other acids of the lichens, it yields

coloured compounds when acted on by alkalies with the aid of the atmosphere; but ammonia is not essential to their production, and they are carmine-red, not purple or blue. Neither does usnic acid yield orcin under any circumstances, so far as we yet know. Its formula is $C_{38}H_{17}O_{14}$, and in combining with bases it loses no water.

Chrysophanic Acid.—In *Parmelia parietina* Rochleder and Heldt discovered another crystallizable acid, which forms fine golden-yellow prisms. With alcoholic solutions of potash and ammonia it yields a magnificent red colour, which acids precipitate gold yellow. The formula of the acid is $C_{10}H_8O_3$, $= \frac{1}{2}$ naphthaline $C_{10}H_8$ + 3 eq. of oxygen. The chrysophanate of potash is dark blue or violet, but dissolves in water with a red colour. Chrysophanic acid has also been discovered in rhubarb by Schlossberger and Doepping.

In his examination of lichens Kane obtained four substances, which, according to his analyses, have the following formulæ:—

Erythryline (Erythric Acid ?)	. . .	$C_{22}H_{16}O_6$
Erythrine (Lecanorate of Oxide of Ethyle ?)	. . .	$C_{22}H_{13}O_9$
Amarythrine (Picroerythrine ?)	. . .	$C_{22}H_{13}O_{14}$
Telerythrine (Picroerythrine ?)	. . .	$C_{22}H_{16}O_{10}$

Except, perhaps, the first, all of these are evidently products of decomposition of the substances present in the lichens. Even the first, if it be really erythric acid, has undergone some change, as it has not the composition of the acid as existing in the lichen. Since the researches of Schunck, Rochleder and Heldt, and Knop, those of Heeren, Robiquet, and Kane can no longer be considered sufficient, as we are now aware how extremely prone to change these substances are. Moreover, the discovery that Heeren's pseudo-erythrine, the erythrine of Kane, is lecanorate of oxide of ethyle, demonstrates the incorrectness of Kane's formula for that substance.

ARCHIL.—CUDBEAR.—LITMUS.

These are the names given to the dye-stuffs prepared in different countries from the lichens above mentioned, by exposing them to the air in contact with putrefying urine or ammoniacal solutions. By this means the colour is developed, and a great part separates as a powder, while some remains dissolved. It is either dried for use, or thickened by the addition of chalk or gypsum.

The best Archil is prepared as above from the *Rocella tinctoria*, which is found in the Canary Islands, the Azores, Corsica, and Sardinia. When a mixture of carbonate of potash and ammonia is employed in the preparation, and chalk, &c. is afterwards added, the co-

lour is rendered more blue by the alkali, and is named Litmus. Cudbear is chiefly prepared in England from *Lecanora tartarea* and *Parmelia omphaloides*. It is called Persio in Germany.

According to Kane, who has lately examined these substances, archil contains two colouring matters, Alpha-orceine and Beta-orceine, which differ only in the proportion of oxygen. The former is $C_{18}H_{10}NO_5$; the latter $C_{18}H_{10}NO_8$. Kane considers beta-orceine to be the same as orceine; but it will be seen that there is a difference between the formulæ of these compounds, as given by Kane and Dumas. Nevertheless, it must be observed that the formulæ of Kane's two varieties of orceine are easily deduced from that of anhydrous orceine, according to Dumas, by the addition of ammonia and oxygen. Anhydrous orceine, according to Dumas, is $C_{18}H_7O_3$. Now, if to this we add $NH_3 + O_5$, we shall have the formula of beta-orceine.

The properties of alpha-orceine and beta-orceine are the same as those of orceine. They have all a deep red colour, are sparingly soluble in water, and are separated from the solution by the addition of a neutral salt. In alkalies they dissolve with a magnificent purple colour.

Besides orceine, archil contains a red substance of an oily aspect, which Kane calls Erythroleic acid; and another compound, called Azoerythrine; besides a yellow matter, noticed by Heeren.

Litmus contains, according to Kane, four distinct compounds; namely, Erythroleine, Erythrolitmine, Azolitmine, and Spaniolitmine.

Erythroleine is liquid at 212° ; soluble in alcohol, ether, and alkalies, with a purple colour. Formula, $C_{26}H_{22}O_4$.

Erythrolitmine is red; sparingly soluble, like the preceding, in water; soluble in hot alcohol. It dissolves in alkalies with a blue colour. Formula, $C_{26}H_{23}O_{18}$.

Azolitmine is insoluble in water and alcohol, soluble in alkalies. It is the chief ingredient of litmus, and corresponds to beta-orceine, from which it differs in containing 2 at. of oxygen more. Formula, $C_{18}H_{10}NO_{10}$.

Spaniolitmine contains no nitrogen. It is rarely present, has a bright red colour, and is soluble in alcohol and ether. Formula, $C_{18}H_7O_{16}$.

According to Kane, the ingredients of archil and litmus are in a continual state of transition, probably from the action of oxygen.

Alpha-orceine and *Beta-orceine*, when dissolved in ammonia, are decolorized by contact with metallic zinc, and an excess of ammonia precipitates white compounds which become purple in the air. They contain oxide of zinc, combined, according to Kane, with alpha-orceine

and beta-orcine. It is probable, however, that the body in combination with the zinc contains less oxygen, as it acquires colour when exposed to the air.

According to Gélis, when litmus is dissolved in weak potash, and the blue solution precipitated by acetate of lead, the precipitate decomposed by sulphuretted hydrogen gives a mixture of sulphuret of lead with three colouring matters. Ammonia separates them from the sulphuret, and the addition of acetic acid precipitates the colouring matters in the form of a fine red powder. Ether extracts from this a reddish orange crystalline substance. From the residue alcohol dissolves a blood-red compound, and leaves a mass insoluble in water, which, when burned, leaves ashes. It dissolves in alkalies with a blue colour. All three contain nitrogen.

The natural colour of the ingredients of archil and litmus seems to be red, but it is turned blue or purple by the presence of alkalies.

These dye-stuffs yield very brilliant but fugitive colours to cloth. They are chiefly used to heighten the bloom of other dyes.

The reader will observe the analogy between the substances now described, and the coloured compounds formed by the action of air and ammonia on salicine and phloridzine as formerly described.

INDIGO.

We shall describe this remarkable substance in the pure state, with the numerous products arising from it, in the first instance; after which the formation of the indigo of commerce will be more easily understood.

To obtain pure indigo, the commercial substance, in fine powder, is placed for several days in contact with green vitriol, hydrate of lime, and water, in a stoppered vessel. The best proportions are 5 parts of indigo, 10 of green vitriol, 15 of hydrate of lime, and 60 of water. The colour is destroyed, and the clear yellowish fluid is drawn off with a syphon, mixed with hydrochloric acid, and the blue precipitate which falls is well washed, first with pure water, and then with boiling alcohol, until the latter solvent no longer acquires any colour, or only a pure blue; it is then dried in the air. Instead of the above mixture a solution of 1 part of caustic soda and 1 of grape-sugar in 20 of water may be employed to dissolve the indigo. Fritzsche has shewn, that if alcohol be used in this experiment instead of water, the indigo is obtained in crystals. If 4 oz. of powdered crude indigo and 4 oz. of grape-sugar are mixed with hot alcohol of 75 per cent. in a 12-lb. bottle, and then a mixture of 6 oz. of concentrated caustic soda ley

with hot alcohol be added, and the bottle entirely filled with hot alcohol, well shaken, and allowed to rest, the clear liquid, when drawn off and exposed to the air, deposits 2 oz. of pure indigo in crystals, which are to be well washed, first with alcohol, and then with hot water, till the mother-liquor is removed. The crystals exhibit a coppery lustre.

Pure indigo forms a deep blue powder, which acquires a coppery lustre when rubbed with a smooth body. It is quite insoluble in water, alcohol, ether, fixed and volatile oils, hydrochloric acid, and diluted alkalies. It dissolves in oil of vitriol with a deep blue colour; and with anhydrous sulphuric acid it forms a reddish purple mass, which dissolves in water without developing heat, and forms a deep blue solution. By the action of nitric, chloric, and chromic acids, of chlorine and bromine, it is changed, becomes yellow, and yields a multitude of new products, which dissolve with a yellow colour in water and alcohol. It is also decomposed when heated with a strong solution of caustic potash. It is decolorized and dissolved by contact with many deoxidizing agents, such as protoxides of iron, tin, and manganese, if a soluble alkaline base be present; and undergoes the same change in contact with alkalies and grape-sugar. In the latter case, formic acid is produced. When thus dissolved, white indigo is formed.

When thrown in small quantity on a heated plate of platinum, indigo is totally sublimed, without charring, in the form of purple vapours which condense into purple crystals. When a large quantity is heated, the lower part is charred, and the crystals which are formed condense on the upper surface, from which they are easily separated.

White Indigo.—To obtain this compound, the yellow alkaline solution above described as prepared from common indigo is carefully protected from the access of air, both before and after the addition of the hydrochloric acid. The precipitate is well washed with recently boiled water, or with diluted sulphurous acid, rapidly drained on a filter, and dried on the filter in the vacuum of an air-pump. When the process is well performed, there is obtained a grey mass, sometimes slightly blue on the surface, which is formed of minute crystals.

White indigo is insoluble in water and diluted acids; soluble in alkalies, alcohol, and ether, to which it gives a yellow colour. When exposed to the air, it becomes blue from the absorption of oxygen; rapidly if moist, more slowly in the dry state: and its solutions, when exposed to the air, deposit blue indigo as a fine powder.

The solutions of white indigo in alkalies precipitate many metallic salts. These precipitates, when they are not blue at first, become so

on exposure to the air. According to Runge, the precipitate formed by white indigo in solutions of sesquioxide of iron yields, when heated, a green crystalline sublimate; that formed with salts of black oxide of copper, a yellow sublimate, also crystalline; that formed in solutions of silver, orange-yellow crystals; and that formed in solutions of binoxide of mercury, grass-green crystals. These sublimates require a more minute investigation, especially as the results of Runge differ from those of other experimenters.

COMPOSITION OF BLUE AND OF WHITE INDIGO.

The first accurate analysis of blue indigo was made by Crum, and has been confirmed by Dumas and by Erdmann. Its formula is $C_{16}H_5NO_2$. White indigo, according to Dumas, is $C_{16}H_6NO_2$; so that they differ only by 1 eq. of hydrogen. Two views may be taken of their relation to one another. According to the first, white indigo is blue indigo *plus* 1 eq. hydrogen; just as hyduret of benzoyle is benzoyle + 1 eq. hydrogen. According to the other, white indigo is the hydrate of a compound containing 1 eq. less oxygen than blue indigo. Thus, blue indigo = $C_{16}H_5N + O_2$, and white indigo = $C_{16}H_5N + O + HO$. They would thus be viewed as oxides of a common radical, $C_{16}H_5N$, the protoxide being hydrated.

The fact, that white indigo is produced by the deoxidizing agency of grape-sugar, speaks strongly in favour of the latter view; for, were white indigo a hyduret of blue indigo, it could only be formed here by the decomposition of water, the hydrogen of which would unite with the blue indigo to form white indigo, while its oxygen would again unite with the hydrogen of the sugar. It is highly improbable that oxygen should quit hydrogen to unite with the same element.

Moreover, white indigo combines with oxides; and, like other substances which do so, it probably combines with basic water when separated from a fixed base. On the whole, therefore, while both views deserve attention, we incline to the latter; and the reader will not fail to remark, that the relation between blue and white indigo is the same, in all probability, as that between alloxan and alloxantine.

Blue indigo contains the elements of cyanogen, and benzoyle or benzile; for benzoyle = $C_{14}H_5O_2$ + cyanogen = C_2N , = $C_{16}H_5NO_2$. It is worthy of remark, that when benzile is heated with caustic potash, an indigo-blue colour is formed, which soon disappears.

ACTION OF SULPHURIC ACID ON INDIGO.

This subject has been investigated by Crum, Berzelius, and Dumas. It has been mentioned that indigo may be made to combine with anhydrous sulphuric acid, or with oil of vitriol. Fuming sulphuric acid also readily dissolves one-fifth of its weight of indigo; and when mixed with water, no insoluble matter is separated. But when 1 part of indigo is dissolved in 8 parts of oil of vitriol, the addition of water separates a purple powder. The filtered solution contains, according to Berzelius, two acids, sulphoindigotic acid and hyposulphoindigotic acid; while the purple powder above mentioned is a third acid, the sulphopurpuric. All these acids yield, with alkalies, blue or purple salts, which are insoluble in saline solutions, but readily soluble in pure water. For this reason, when the acid solution of indigo is neutralized with acetate or carbonate of potash, the salts of potash separate as a bulky blue precipitate, which is called blue carmine or soluble indigo. The salts of hyposulphoindigotic acid are more soluble than those of sulphoindigotic acid.

When separated by means of sulphuretted hydrogen from their compounds with oxide of lead, these two acids are yellow and soluble in water, and their solutions absorb oxygen from the air, becoming blue.

When sulphoindigotate of potash is dissolved in 50 parts of lime water, and heated with contact of air, the solution becomes first purple, afterwards scarlet, and lastly pure yellow. According to Berzelius, these colours are owing to the successive production of four acids, which may be separated at the proper stages of the process. The first he calls purpurosulphuric, the second flavosulphuric, the third fulvosulphuric, and the fourth rufosulphuric acid. These compounds require a thorough investigation.

All the blue acid solutions just described, as well as their salts, are turned yellow by nitric acid, chlorine, and bromine.

The sulphopurpuric acid, (Phœnicine of Crum,) when well washed, dissolves in water with the same blue colour as the other two; but gives purple salts with bases, of which the salts of soda and ammonia are the most soluble.

According to Dumas, the action of sulphuric acid on indigo is analogous to its action on alcohol. The indigo loses 1 atom of water, and the residue combines with 2 atoms of sulphuric acid. The acid thus formed he calls sulphindylic acid, and compares it to sulphovinic acid, and the organic compound in it to oxide of ethyle (ether). According to this view, blue indigo is the hydrate of an organic oxide,

$C_{16}H_4NO + HO$; sulphindylie acid is $C_{16}H_4NO + 2SO_3 + HO$, and the salt of potash is $C_{16}H_4NO, SO_3 + KO, SO_3$. But, as it is impossible in any way to reproduce indigo from these compounds, as alcohol may be reproduced from sulphovinic acid and its salts, this view is not very probable.

Moreover, if such be the composition of blue indigo, it is hardly possible to account for the production of white indigo, according to any known analogies.

The opinion is therefore much more probable, as well as more consonant to analogy, that the acids formed by the action of sulphuric acid on indigo contain, not sulphuric, but hyposulphuric acid, as is the case with isethionic and other acids.

According to Dumas, the sulphopurpuric acid is composed of 2 atoms indigo and 2 atoms sulphuric acid, which together neutralize 1 atom of base.

The whole subject of these acid compounds is still exceedingly obscure, and must continue so until further investigations shall have been made.

PRODUCTS OF THE OXIDATION OF INDIGO.

Isatine.—This remarkable compound is one of the products obtained when indigo is oxidized by means of sulphuric acid and bichromate of potash. It was discovered at the same time by Erdmann and by Laurent.

To obtain it, indigo, mixed with water to a thin paste, is gently warmed and nitric acid added in small portions, allowing the effervescence caused by each addition to be over before adding the next portion, till the blue colour is destroyed; avoiding, however, the addition of more acid than is necessary for this purpose. A brown deposit is obtained. A large quantity of water is now added, and boiled with the mass; the filtered solution on cooling deposits isatine in crystals. These are purified by dissolving them in potash, and adding hydrochloric acid as long as it causes a black or brown precipitate of resinous matter. When a filtered portion gives with hydrochloric acid a pure bright red precipitate, the whole is filtered and mixed with the acid, which causes the isatine to fall as a red crystalline powder. This is to be well washed with cold water, and crystallized by solution in hot alcohol.

Isatine forms hyacinth-red or reddish-orange crystals, of a brilliant lustre, easily soluble in hot water and in alcohol. Its solutions stain the skin, and give it a disagreeable odour. It is decomposed by heat. Chlorine converts it into two new compounds, chlorisatine and bichlorisatine. When dissolved in alkalis, it is changed into isatinic acid

According to Erdmann and Laurent, its formula is $C_{16}H_5NO_4$; so that it represents blue indigo *plus* 2 atoms of oxygen.

Isatinic Acid.—Isatine dissolves in caustic potash with a purple colour, which passes into yellow on the application of heat. The fugitive purple colour belongs to a compound of isatine with potash; and an analogous compound with oxide of silver, which is red and gelatinous, is formed when the purple compound is mixed with salts of silver. The liquid yields, on evaporation, isatate of potash as a crystalline salt, which, when recrystallized from alcohol, forms small, hard, colourless prisms. This salt gives with acetate of lead a white precipitate, isatate of lead; which, when decomposed by sulphuretted hydrogen, yields a solution of the acid. Isatinic acid is deposited from this solution by spontaneous evaporation as a white powder, hardly crystalline.

It is soluble in cold water; but the solution when heated becomes yellow, owing to the production of isatine. The formula of the anhydrous acid in the salt of silver is $C_{16}H_6NO_5$, and it represents isatine *plus* 1 atom of water. It is therefore formed from isatine as benzoic acid is from benzoic, but the atom of combined water is more easily separated.

According to Laurent, isatine forms with ammonia a salt, the acid of which contains 3 at. isatine + 2 at. water.

Isatinosulphites.—Sulphurous acid has no action on isatine, but when a current of the gas is passed through a solution of isatinate of potash, there is formed a new salt, isatinosulphite of potash, composed of 1 eq. of isatine, 2 eq. of sulphurous acid, and 1 eq. of potash, which yields sulphur-yellow crystals, very soluble in water. A similar salt of ammonia has been formed. (Laurent.)

Isatyde.—When isatine is dissolved in hydrosulphuret of ammonium, there is deposited, on cooling, a yellowish-white powder, not crystalline, which Erdmann calls Isatyde. It dissolves in ammonia and in the caustic alkalis with a dark red colour, which passes into yellow on the application of heat. The solution in potash deposits crystals, and gives with hydrochloric acid a flocculent yellow precipitate.

The formula of isatyde is $C_{16}H_6NO_4$, which readily explains its formation, since it is isatine + 1 eq. of hydrogen. (Laurent.)

Sulphésatyde.—This compound is formed when sulphuretted hydrogen is passed through a boiling saturated solution of isatine in alcohol. Sulphur is deposited, mixed with the crystals of the new compound. The addition of water to the liquid precipitates the whole of the sulphésatyde. When dry, it is greyish-yellow, tasteless, inodo-

rous, insoluble in boiling water, in which it softens. Its formula is $C_{16}H_6NO_2S_2$, so that it is isatyde in which 2 eq. of oxygen have been replaced by 2 eq. of sulphur.

Sulphasatyde.—When caustic potash is added drop by drop to an alcoholic solution of sulphésatyde, the liquid becomes red, and on standing deposits a crystalline white precipitate of sulphasatyde. It has sometimes a tint of rose-colour, from the presence of a little *indine*, the compound next to be described. The formula of sulphasatyde is $C_{16}H_6NO_3S$, and it is therefore isatine in which only 1 eq. of oxygen has been replaced by sulphur.

Indine.—When sulphésatyde is rubbed in a mortar with concentrated potash, the mixture acquires a rose-colour, and if alcohol be now added by degrees, the mixture being constantly stirred, this colour becomes very pure and intense. The powder which is deposited is then well washed, first with alcohol, and finally with water.

To purify it, a little alcohol is now poured on the moist powder, and when it has drained, it is covered in a basin with a lukewarm very strong solution of potash, in which it instantly dissolves, forming a black liquid, which in a few seconds becomes a thick mass of black needles. If the potash be too warm, the black colour disappears, and the indine is then totally destroyed. The black crystals are washed, first with alcohol, then with a few drops of weak hydrochloric acid, and, lastly, with water. In the course of the washing the black crystals are changed into pure indine. It may be obtained in crystals, by dissolving the black crystals in alcohol and adding hydrochloric acid. It is decomposed by boiling with nitric acid; and with bromine it yields new compounds, to be afterwards mentioned. With potash it also forms new compounds.

The formula of indine is $C_{16}H_6NO_2$, so that it is sulphésatyde minus 2 eq. of sulphur, and is also isomeric with white indigo. It may be obtained from isatyde by the action of potash, along with isatinic acid of potash. 3 eq. of isatyde + 2 eq. of potash correspond to 2 eq. of isatinic acid of potash and 1 eq. of indine. $3(C_{16}H_6NO_4) + 2KO = 2(C_{16}H_5NO_4, HO, KO) + C_{16}H_6NO_2$.

Indinic Acid.—This is the acid contained in the black crystals above mentioned. It is formed apparently from indine, as isatinic acid is from isatine, by the assimilation of 1 eq. of water, but it is resolved into indine and water when we attempt to separate it. Its formula is probably $C_{16}H_6NO_2 + HO$.

Hydrindine.—When sulphasatyde is acted on by potash, there are formed small brilliant yellow crystals of Hydrindine, and similar but more silky crystals of a compound of hydrindine with potash. They

are washed with water, which removes the potash, and leaves pure hydrindine. The same compound is formed when the black solution of indine in potash is too strongly heated.

Hydrindine is yellow, crystalline, insoluble in water; it is converted by boiling nitric acid into *nitrindine*. It is converted into indine by a heat of 572° , which is easily explained by its formula, which is $C_{32}H_{13}N_2O_5$ that is, 2 eq. indine + 1 eq. water.

With potash, hydrindine forms, like isatine and indine, a salt, the acid in which is hydrindine + water, and when separated from the alkali, it is reconverted into hydrindine. (Laurent.)

Nitrindine.—When indine or hydrindine is acted on by hot nitric acid, it is converted into a brilliant violet powder, insoluble in water, sparingly soluble in alcohol and ether. Its formula is $C_{16}H_4N_2O_7 =$

$C_{16} \left\{ \begin{matrix} H_4 \\ NO_4 \\ O \end{matrix} \right\} NO_2$; that is, indine in which 2 eq. of hydrogen have been

replaced, one by nitrous acid, the other by oxygen. (Laurent.) It seems to form an acid of little stability when in contact with potash, like the preceding compounds.

Sulphisatanous Acid.—When sulphésatyde is acted on by bisulphite of ammonia, several substances are formed, one of which is soluble, the others insoluble. The soluble compound is a crystallizable salt, the sulphisatanite of ammonia. It is quite distinct from isatinosulphite of ammonia. Its formula appears to be $C_{16}H_6NO_3, 2SO_2 + NH_4O + 2$ aq. (Laurent); but, according to Hofmann, it is more probably $C_{16}H_6N \left\{ \begin{matrix} O_2 \\ 2SO_2 \end{matrix} \right\} + NH_4O + 2$ aq., in which formula 2 eq. of oxygen in sulphésatyde have been replaced by sulphurous acid. This would account for the fact that strong acids do not disengage sulphurous acid from it, that acid not playing the part of an acid in this compound. Laurent succeeded in separating the acid, which forms small needles; but his analysis does not agree well with his formula.

Isatane.—The insoluble matter formed along with the preceding compound is composed partly of indine, but chiefly of isatane, which is a white powder, resolved by heat into isatine and indine. Its formula is $C_{16}H_6NO_3$; and 3 eq. of it yield, when heated, 1 eq. of isatine, 2 eq. of indine, and 1 eq. of water. $3(C_{16}H_6NO_3) = C_{16}H_5NO_4 + 2(C_{16}H_6NO_2) + HO$.

Indine and nitrindine also form new compounds when treated with bisulphite of ammonia, but these have not yet been investigated.

ACTION OF CHLORINE ON ISATINE, ETC.

When a solution of isatine is saturated with chlorine, two new compounds are obtained, which only differ from isatine in having a part of the hydrogen replaced by chlorine. They are called Chlorisatine and Bichlorisatine. Both are hardly soluble in cold water, and are separated by alcohol, in which the latter is rather more soluble than the former. Both these compounds are also formed by the direct action of chlorine on indigo, in which case isatine is probably first produced, and then decomposed by the chlorine.

Chlorisatine.—Formula $C_{16}H_4ClNO_4$. It crystallizes from alcohol in transparent four-sided prisms of an orange colour and a bitter taste. It may be partly sublimed. It dissolves in 50 parts of hot water. Sulphuric acid dissolves it without decomposition; nitric acid destroys it. It causes no precipitate of chloride of silver in solutions of that metal.

Chlorisatinic Acid.—Chlorisatine is acted on by caustic potash exactly as isatine is. It dissolves at first with a deep red colour, which passes into yellow; and the solution deposits a bright yellow salt, the chlorisatinate of potash. The acid, when separated from its salts, is instantly resolved into chlorisatine and water. Its formula, $C_{16}H_5ClNO_5$, explains this, as it is equivalent to chlorisatine + 1 atom of water. The salt of potash gives, with the solutions of silver and baryta, yellow crystalline salts; with solutions of lead, a brilliant yellow gelatinous precipitate, which shortly changes into a scarlet crystalline powder. The latter dissolves in hot water, and is deposited again in red crystals.

Bichlorisatine.—Formula, $C_{16}H_3Cl_2NO_4$. It forms small hyacinth-red crystals, rather more soluble in water and alcohol than chlorisatine, which it resembles very much in its characters.

Bichlorisatinic Acid.—It is formed exactly as chlorisatinic and isatinic acids are, by the action of caustic potash on bichlorisatine. The bichlorisatinate of potash is yellow; as are the salts of baryta, silver, and lead, the latter permanently so. The salt of copper is, when first formed, of the colour of hydrated peroxide of iron; it then becomes pale greenish yellow, and finally carmine-red.

Bichlorisatinic acid is more permanent than chlorisatinic acid, and may be obtained from the salt of potash as a yellow powder. But when its solution is heated, or evaporated to dryness, the acid is resolved into its component parts, bichlorisatine and water. Formula $C_{16}H_4Cl_2NO_5$, = bichlorisatine $C_{16}H_3Cl_2NO_4$ + 1 at. water HO.

By the action of bromine on isatine there are formed two new compounds, *bromisatine* and *bibromisatine*, analogous in composition and properties to the preceding. Bibromisatine, treated with potash, yields *bibromisatinic acid*.

It is to be observed that the action of chlorine on isatine is very analogous to its action on salicylous acid, and it is probable that the action of ammonia on the compounds thus produced will yield results similar to those obtained from the action of ammonia on the chloride of salicyl.

Chlorisatyde.—When chlorisatine is dissolved with the aid of heat in hydrosulphuret of ammonium, the solution deposits, on cooling, a white or yellowish powder, hardly crystalline. This is called, by Erdmann, *Chlorisatyde*. It is sparingly soluble in water, and by heat is resolved into chlorisatine, water, and a new compound, *Chlorindine*, which appears as a violet powder. The formula of chlorisatyde is $C_{16}H_5ClNO_4$; that of chlorindine is $C_{16}H_5ClNO_2$.

Chlorisatyde dissolves in potash with a red colour, which passes into yellow; and the liquid now yields, on evaporation, a salt composed of potash and a new acid, *Chlorisatydic acid*.

Bichlorisatine, treated with hydrosulphuret of ammonium, yields analogous results, producing *bichlorisatyde*; and, from the action of potash on this, *bichlorisatydic acid*.

Bibromisatine, acted on by sulphuret of ammonium, yields *bibromisatyde*. Both this compound and bichlorisatyde are decomposed by heat in the same way as chlorisatyde, yielding, along with bichlorisatine and bibromisatine, two new compounds, *bichlorindine*, very similar to chlorindine, and *bibromindine*, which is deep red, nearly black, and dissolves in alcohol with a fine purple colour.

By the action of alcohol, saturated with sulphuretted hydrogen, on isatine and chlorisatine, Erdmann obtained two new compounds, which he calls *Sulphisatyde* and *Sulpho-chlorisatyde*. Their composition is not ascertained.

The action of potash on isatyde appears to be the type of its action on chlorisatyde, bromisatyde, bichlorisatyde, and bibromisatyde. When isatyde is acted on by potash, it yields isatine (or isatinate of potash), indine (or indinate of potash), and hydrindine (or hydrindinate of potash). 6 eq. isatyde $6(C_{16}H_6NO_4)$ are equal to 4 eq. isatine $4(C_{16}H_5NO_4)$ + 2 eq. indine $2(C_{16}H_6NO_2)$ + 4 eq. water: or they are equal to 4 eq. isatine $4(C_{16}H_5NO_4)$ + 1 eq. hydrindine $(C_{32}H_{13}N_2O_5)$ + 3 eq. water. Both changes probably occur, and the three compounds, isatine, indine, and hydrindine, alike take up the elements of water to form the acids, which, to avoid confusion,

are not here expressed. Now there is good reason to believe that precisely analogous changes occur when potash acts on bichlorisatyde and on bibromisatyde, each yielding three corresponding compounds and the three acids derived from these. The reader, by strictly following the analogy of the formulæ given above for the action of potash on isatyde, will easily be able to construct the equations for the other analogous cases.

Chloranile.—By the action of chlorine on a warm alcoholic solution of chlorisatine or bichlorisatine, Erdmann obtained a new compound of carbon, oxygen, and chlorine, which he calls Chloranile. Its formula is $C_{12}O_4Cl_4$. It forms pale yellow pearly scales, soluble in hot alcohol, unaltered by acids, fusible and volatilizable without decomposition. When dissolved in caustic potash, half of its chlorine is replaced by oxygen, and *chloranilic acid* is formed, the formula of which is C_6O_3Cl . Chloranile dissolves in sulphuret of potassium, forming a yellow solution; which, when exposed to the air, passes through all shades of red, till at last it becomes purple and opaque from the separation of a black powder. Hofmann has shewn that chloranile is a very frequent product of the action of chlorine on bodies belonging to the series of indigo, as well as to those of phenyle and salicyl, having obtained it from aniline, isatine, chlorisatine, hydrate of phenyle, nitrophenisic and nitrophenesic acids, hyduret of salicyl, salicine, anthranilic acid, and other substances. Like aniline, it evidently belongs to the series of phenyle, to which the other series are reduced.

Chloranilic Acid.—A hot solution of chloranile in potash deposits, on cooling, brownish purple brilliant prisms of chloranilate of potash. A solution of this salt, mixed with hydrochloric acid, gives reddish white shining scales of hydrated chloranilic acid, the formula of which is $C_6O_3Cl.HO + aq$. The solutions of the salts of this acid are commonly purple.

Chloranilammon and *Chloranilam*.—Chloranile dissolves in ammonia with a blood-red colour, and the solution yields crystals of *chloranilammon*. They are small chesnut-brown needles, which dissolve in hot water, tinging it purple. When this solution is mixed with hydrochloric acid, it does not yield chloranilic acid, but black needles of *chloranilam*.

The former compound contains the elements of 1 at. chloranilic acid and 1 at. ammonia, and in the crystals 4 at. of water of crystallization. The latter contains the elements of 2 at. of chloranilic acid, 1 at. of ammonia, and 5 of water of crystallization. They cannot be considered as salts of ammonia, for they do not contain, in the anhy-

drous state, the elements of water necessary to form oxide of ammonium; neither do they contain chloranilic acid, for their reactions with metallic salts are quite different from those of a chloranilate. By the action of alkalis they are changed into chloranilates, while ammonia is disengaged; and, when heated with mineral acids, they likewise yield ammoniacal salts, while chloranilic acid is separated.

When the product of the action of chlorine on an alcoholic solution of chlorisatine or bichlorisatine, after the chloranile has been separated, is subjected to distillation, there remains a brown resinous mass, which, on being further heated, yields a semifluid oily product, often accompanied with a white crystalline sublimate. If the whole product be now redistilled with aqua potassæ, a solid substance is volatilized, and the residue dissolves. The solution deposits prismatic crystals, which are purified by repeated crystallizations from aqua potassæ. The solution of this salt, mixed with hydrochloric acid, yields a white flocculent precipitate, which volatilizes with the vapours of boiling water, and sublimes in needles. This compound is similar to one obtained by Erdmann among the products of the action of chlorine on indigo. He calls it *Chlorinized Chlorindoptenic Acid*; and, from the analysis of the salt which it forms with oxide of silver, he deduces the remarkable formula, $C_{12}Cl_5$, for the anhydrous acid. But Laurent has shewn that the true formula of the acid is $C_{12}Cl_5O,HO$, and that it is identical with his chlorephenusic acid.

PRODUCTS OF THE ACTION OF CHLORINE ON INDIGO.

According to Erdmann, when powdered indigo, mixed with water, is exposed to the action of chlorine at a low temperature, it is completely decomposed, and yields an orange or brownish mass. When the whole is distilled, a white crystalline sublimate is obtained, which is a mixture of two new compounds, *Chlorindatmit* and *Chlorindoptenic Acid*. The residue, boiled with water, yields a large quantity of chlorisatine and bichlorisatine, and there remains a resinous mass. The liquid, out of which the chlorisatine and bichlorisatine have crystallized, is acid from free hydrochloric acid, and contains sal-ammoniac.

Chlorindatmit. Syn. Trichloraniline.—When the mixed sublimate above described is distilled with carbonate of potash, chlorindatmit is obtained as a white sublimate, fusible and volatile, having an odour of fennel. Formula, $C_{12}H_4Cl_3N$.

This compound is derived from aniline, $C_{12}H_7N$, by the replacement of 3 eq. of hydrogen by 3 eq. of chlorine. (Hofmann.)

Chlorindoptenic Acid. Syn. Chlorophenusic Acid.—This acid re-

mains combined with the potash, forming a crystallizable salt, which, when acted on by acids, yields chlorindoptenic acid in white flocks, of a nauseous smell. Its formula is $C_{12}H_2Cl_3O + HO$, and it is identical with the chlorophenisic acid of Laurent. It forms with oxide of silver a lemon-yellow insoluble salt, $C_{12}H_2Cl_3O + AgO$.

Erdmann gave to the mixed sublimate, containing the two preceding compounds, the name of *Chlorindoptene*. It appears to be a mixture of the two in variable proportion.

It is obvious that the action of chlorine on indigo is analogous to that of chromic acid already described, with the exception that the isatine, as might be expected, is converted into chlorisatine and bichlorisatine. It is not known whether the chlorindatmit and chlorindoptenic acid are formed directly from indigo, or by the action of hydrochloric acid and chlorine on chlorisatine and bichlorisatine.

ACTION OF AMMONIA ON ISATINE.

By the action of ammonia on isatine there are produced several new compounds, varying with the strength of the ammonia and the menstruum employed. In these compounds oxygen is replaced by *amide*, NH_2 , or *imide*, $\frac{1}{2} NH = Im$.

Imesatine is formed when dry ammonia is passed through an alcoholic solution of isatine. It forms fine deep yellow crystals, the formula of which is $C_{16}H_6N_2O_2 = C_{16}H_5N \left\{ \begin{matrix} O_2 \\ 2\ Im \end{matrix} \right.$.

Imasatine is formed when aqua ammoniæ acts on a solution of isatine in alcohol. It is a greyish yellow crystalline substance, the formula of which is $C_{16}H_5N \left\{ \begin{matrix} O_3 \\ Im \end{matrix} \right. ?$

Imasatinic Acid is formed along with the preceding, and is dissolved along with ammonia. By the addition of an acid it is precipitated as a beautiful scarlet crystalline powder, soluble in hot alcohol, which deposits it in splendid tabular crystals, similar to the sublimed periodide of mercury. It dissolves sparingly in acids with a violet colour, and these solutions deposit violet crystals. Its formula is $C_{16}H_5N \left\{ \begin{matrix} O_3 \\ Im \end{matrix} \right\} + HO$.

Amasatine is formed along with the two preceding bodies. It has a fine yellow colour, and dissolves in acids with a violet colour, apparently passing into imasatinic acid. Its formula is $C_{16}H_5N \left\{ \begin{matrix} O_3 \\ Ad \end{matrix} \right\} + HO$.
($Ad = NH_2 = amide$.)

The analogy between chlorisatine, &c., and isatine, holds in regard to

the action of ammonia on them. By the action of dry ammonia on an alcoholic solution of chlorisatine there is formed a yellow crystalline compound, analogous to imesatine. It is called *Imechlorisatinase*, and its formula is $C_{16} \left\{ \begin{smallmatrix} H_4 \\ Cl \end{smallmatrix} \right\} N \left\{ \begin{smallmatrix} O_2 \\ Im_2 \end{smallmatrix} \right\}$.

Imachlorisatinase is analogous to imasatine. Its formula is $C_{16} \left\{ \begin{smallmatrix} H_4 \\ Cl \end{smallmatrix} \right\} N \left\{ \begin{smallmatrix} O_3 \\ Im \end{smallmatrix} \right\}$. It forms brownish yellow crystals.

Imabromisatinase, formed by the action of dry ammonia on bibromisatine in alcohol, is $C_{16} \left\{ \begin{smallmatrix} H_3 \\ Br_2 \end{smallmatrix} \right\} N \left\{ \begin{smallmatrix} O_3 \\ Im \end{smallmatrix} \right\}$. It is a deep orange crystalline powder.

We have now briefly run over the catalogue of the very remarkable compounds derived from indigo by the action of sulphuric acid and bichromate of potash, which produces isatine, and by the action of chlorine either on indigo or on isatine, of bromine on the same, and of potash, ammonia, sulphuretted hydrogen, and sulphuret of ammonium on the products of these actions. The nomenclature of these compounds is in a very imperfect state, and requires reformation; but this cannot be effected until the substances themselves have been more thoroughly studied. It is most important to observe, that by or through chloranile and the chlorindoptenic acids, the series to which indigo belongs connects itself with that of carbolic acid or hydrate of phenyle, (to be afterwards described;) and these, again, with the series of salicyle. We have now to mention one or two products of the action of nitric acid on indigo which are common to all these series, and, like chloranile, seem likely to be very frequently met with as products of the decomposition of organic compounds.

PRODUCTS OF THE ACTION OF NITRIC ACID ON INDIGO.

Anilic Acid. Syn. Indigotic Acid; Nitrosalicylic Acid.—This acid is formed when indigo is gradually added to boiling nitric acid, previously diluted with 12 or 15 parts of water. It is contaminated at first with an acid, oily-looking compound, and is purified by adding acetate of lead to the hot solution as long as it yields a brown precipitate. The filtered liquid deposits anilate of lead; which, when acted on by sulphuric acid, yields pure anilic acid.

It forms fine needles, colourless or yellowish white, which are fusible and volatilizable. Nitric acid converts it into oxalic and carbazotic acids. It requires 1000 parts of cold water for solution, but is far more soluble in hot water. Its formula, according to Dumas, is $C_{14}H_4NO_9$.

+ HO. It forms soluble and crystallizable salts with ammonia, and with the oxides of lead and silver.

Picric Acid. *Syn. Nitropicric Acid; Carbazotic Acid; Nitrophenisic Acid.*—This acid is formed by the action of strong nitric acid, either on indigo, or on the preceding acid. It is also produced by the action of strong nitric acid on salicine, coumarine, silk, and some other substances.

One part of indigo is cautiously added, in very small portions, for fear of explosion, to 10 or 12 parts of hot nitric acid, of sp. gr. 1.43. The mixture is boiled, if necessary, with more nitric acid, till red fumes no longer appear; and, on cooling, impure picric acid is deposited. It is purified by solution in potash and precipitation by nitric acid, and finally by recrystallization from water.

It forms bright yellow scaly crystals, sparingly soluble in cold, easily in hot water; soluble in alcohol and ether. It has a very intense bitter taste. It is fusible and volatilizable when gently heated; but, when rapidly heated it deflagrates.

According to Dumas and Marchand, the formula of the crystallized acid is $C_{12}H_2N_3O_{13} + HO$.

The salts of picric acid explode when heated, frequently with evolution of light. They are bitter when soluble, and the picrate of potash has been used with success as a cure for intermittent fever. They have all likewise a yellow colour; and their general formula is $C_{12}H_2N_3O_{13} + MO$.

When the soluble picrates are left in contact with water, hydrate of lime, and green vitriol, they are decomposed, yielding a blood-red solution, which contains lime united with a new acid, the salts of which, with the alkalies, are soluble, bitter, and yield blood-red solutions.

A solution of picric acid in alcohol is used as a test for potash. If there be not too much water present, the picrate of potash, being very sparingly soluble, is deposited as a yellow crystalline precipitate; whereas the picric acid forms a very soluble salt with soda, and thus serves to distinguish these two alkalies from each other.

PRODUCTS OF THE ACTION OF ALKALIES ON INDIGO.

When powdered indigo is added to boiling aqua potassæ, sp. gr. 1.45, it is easily dissolved, forming a deep reddish brown solution; which, when further evaporated, forms, on cooling, a solid crystalline mass. This dissolves in water; and the solution, when exposed to the air, deposits blue indigo. If the greater part of the potash in the freshly-made solution be neutralized by adding an acid as long as a bluish green

precipitate is formed, there remains a golden-yellow solution, which, when filtered and acidulated with acetic acid, yields a kermes-coloured precipitate. This is called by Fritzsche *Chrysanic Acid*. It is purified by solution in ether, which, when evaporated, leaves it as a yellow mass. When boiled with diluted mineral acids, the solution becomes purple, deposits bluish black crystals, the nature of which is not yet ascertained; while a new acid, Anthranilic Acid, remains in solution. As chrysanic acid has not yet been obtained in a state of purity, its true formula is unknown.

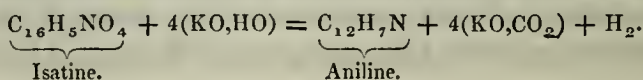
Anthranilic Acid.—This acid is prepared by dissolving indigo in hot aqua potassæ, sp. gr. 1.35, and adding to the mixture powdered peroxide of manganese, till the liquid, when diluted and exposed to the air, no longer forms blue indigo. The solution now contains anthranilate of potash, with a large excess of free potash. It is neutralized by sulphuric acid, and the anthranilate separated from the sulphate of potash by alcohol, which dissolves the former. The salt is decomposed by acetic acid, and yields impure anthranilic acid in orange crystals. It is now combined with lime; and, the anthranilate of lime being purified by recrystallization, its hot solution is decomposed by acetic acid, and, on cooling, deposits hydrated anthranilic acid in tabular crystals half an inch in length, which are nearly colourless.

Anthranilic acid is fusible, and sublimes when gently heated, yielding crystals very similar to benzoic acid. When mixed with powdered glass and strongly heated, it is decomposed, and yields carbonic acid and an oily substance, *Aniline*, which is an organic base, and contains no oxygen. (See the section on the Organic Bases.) Anthranilic acid is sparingly soluble in cold water, soluble in alcohol and ether.

Its formula, according to Fritzsche, is $C_{14}H_6NO_3 + HO$. It forms with lime a salt which crystallizes in large transparent rhombs; and with oxide of silver, a salt, $C_{14}H_6NO_3 + AgO$, which is soluble in hot water and crystallizes on cooling.

Indigo, in being converted into anthranilic acid, loses 2 atoms of carbon, and takes up the elements of 1 atom of water. What becomes of the carbon is not known.

When indigo is distilled with fused potash, *aniline* is obtained. This substance will be described among the organic bases; but it may be here mentioned, that, besides being formed from anthranilic acid, as above shewn, aniline is produced in a variety of other circumstances, and more especially, as Hoffmann has proved, by heating isatine with potash. The action is represented by the following equation:—



Hoffmann, pursuing this train of research, discovered that chlorisatine, bichlorisatine, bromisatine, and bibromisatine, when heated with potash, yield compounds analogous to aniline, but containing chlorine or bromine in the place of a part of the hydrogen. Several of these compounds are basic, and will be mentioned among the organic bases. They all belong, like aniline, to the series of phenyle.

COMMERCIAL INDIGO.

Indigo is obtained from many plants; as from the different species of *Indigofera*, *I. tinctoria*, *I. anil*, *I. argentea*, &c.; from *Wrightea* (*Nerium*) *tinctoria*, *Isatis tinctoria* or woad, *Pegulariat tinctoria*, *Gymnema tingens*, *Polygonum tinctorium*, *Tephrosia* (*Galega*) *tinctoria*, *Amorpha fruticosa*, &c.

In the plants indigo exists in the form of white indigo, and may be extracted in that form by water, alcohol, and ether. It is probably combined with a base, to which it owes its solubility.

In North America the dried leaves are exhausted by warm water, and the infusion exposed to the air, when it deposits blue indigo. In India and South America the fresh or half-dried plants are covered with water and allowed to ferment, when ammonia and carbonic acid are disengaged in abundance, and all the indigo is brought into the soluble state. As soon as a blue or coppery film appears on the surface of the water, it is drawn off, and agitated in open vessels till the blue indigo is deposited as a sandy powder. The powder is dried, and sold in the form of brittle cakes, easily reduced to powder, which, when rubbed with the nail, assume a copper colour. The stronger this colour is, the greater is the proportion of pure indigo present in the specimen examined.

It is never quite pure; and contains the following substances, besides blue indigo, according to Berzelius:—1. *Gluten of indigo*, which is dissolved out by diluted acids. 2. *Indigo-brown*, dissolved by caustic potash with the aid of a gentle heat; it resembles humic and apocrenic acids. 3. *Indigo-red*, which is dissolved, after the removal of the two preceding substances, by boiling alcohol. When heated, this substance yields a white sublimate, *deoxidized indigo-red*, which is reconverted into indigo-red by the action of nitric acid.

When these have been removed, indigo-blue remains, which is still impure, containing mineral substances. It is purified, as before described, by converting it into white indigo, dissolved in an alkali, and pouring the solution into diluted hydrochloric acid, when pure indigo-blue is deposited.

When indigo is distilled, it yields, according to Unverdorben, among

a variety of other products, a substance called by him *Crystalline*, which is a base. (See *Aniline*.)

For dyeing, indigo is dissolved, as before described, either by means of hydrate of lime, green vitriol, and water, or by caustic soda, grape-sugar, and water. In both cases it is converted into white indigo, which dissolves in the alkali with a wine-yellow colour. The cloth to be dyed is steeped in this solution, and exposed to the air; and the process is repeated till the desired depth of colour is attained. Other substances may be used to effect the reduction and solution of the indigo, such as bran and pearlash, or orpiment, lime, and pearlash. The indigo vat, as it is called, is improved by the addition of woad (which itself contains a little indigo, and was used for dyeing blue in Europe before the introduction of the latter) and of madder. An indigo vat, once set in action, may be kept so for several months by the occasional addition either of indigo or of the alkalies and reducing agents, according as one or the other is exhausted.

The solution of indigo in sulphuric acid is also used in dyeing, under the names of *Saxon-blue* and *Soluble indigo*. The finest colour is obtained from the sulpho-indigotate of potash, acidulated with sulphuric acid.

The only method that can be at all depended on for ascertaining the relative values of different specimens of commercial indigo, is to ascertain the weight of the residue left, after the gluten, indigo-brown, and indigo-red have been removed by the successive action of boiling water, diluted acid, strong aqua potassæ with a gentle heat, and boiling alcohol, the action of the latter being repeated till it begins to acquire a pure blue colour. The residue contains only a small portion of mineral impurities. All other methods, such as that of bleaching by chlorine, give most inaccurate results.

COCHINEAL-RED.—CARMINE.—KERMES.

Cochineal is the well-known dye-stuff, which is, in fact, an insect, (*Coccus cacti*,) found on the leaves of a species of cactus in South America. It occurs in small round masses, nearly black, and covered with a fine white powder, which is said to be a sign of good quality.

The colouring principle, *cochineal-red*, or *cochenilline*, forms crystalline grains of a reddish purple, soluble in water and alcohol, insoluble in ether. The aqueous solution is turned orange by acids, violet by alkalies, and yields a beautiful lake with alum, which is known by the name of Carmine. The colour of carmine is heightened by the addition of a solution of tin.

Cochenilline contains nitrogen, but its true formula is unknown.

Prcisser states that the red colouring matter, like all vegetable colours, is derived by oxidation from a colourless crystalline compound, which he calls *carmine*. To the red compound he gives the name *car-méine*. He has analyzed neither. It may here be mentioned that Prcisser has succeeded in isolating the colourless compounds (from which, as he states, the colours are derived by oxidation, especially with the aid of ammonia) in most of the red and yellow dye-stuffs, such as Brasil-wood, safflower, sandalwood, quercitron, woad, annatto, fustic, &c. He obtains them by forming lakes of the colours with oxide of lead, decomposing the lakes by sulphuretted hydrogen, which deoxidizes the colouring matter, when the colourless basis is dissolved, and obtained in crystals by evaporating rapidly, or in vacuo, to avoid oxidation. He has analyzed some of these compounds, but his results are not yet complete.

The finest crimson and scarlet dyes are made from cochineal, according as the mordant is alumina or tin.

Kermes is a dye-stuff similar in its origin and properties to cochineal, but inferior in beauty of tint. It is derived from *Coccus ilicis*.

The red colouring matter of stick-lack, which is also used as a dye, has similar properties. Lac is produced on certain plants by the puncture of an insect.

ALOES.

This well-known drug is the inspissated juice of various species of *aloe*, and contains an azotized compound, distinguished from all others by its relation to nitric acid.

Commercial aloes dissolves readily in hot water and alcohol. The active principle has only been obtained in the form of a yellow extract, which in the original mass appears to be mixed with a brown matter of a resinous aspect, which, however, is soluble in hot water. Further experiments are required to ascertain the true nature of the natural ingredients of aloes; and it is highly probable that the resinoid portion is a product of the action of oxygen on the part which is soluble in cold water, and is believed to be the active principle.

ACTION OF NITRIC ACID ON ALOES.

When nitric acid is made to act on aloes with the aid of heat, a series of new compounds is formed, differing according to the concentration of the acid. Braconnot discovered one of these, namely *Polychromic acid*; and Schunck obtained, besides, two others, *Chrysamic acid* and *Chrysoleipic acid*.

Polychromic Acid. Syn. Artificial bitter principle of Aloes.—To obtain this acid, 1 part of aloes is heated with 8 parts of nitric acid, sp. gr. 1.25. When the reaction is over, the whole is evaporated to the consistence of syrup, and mixed with cold water, which throws down impure polychromic acid. It is purified by washing with water till the liquid passes through of a pure purple colour.

When pure, it forms a yellow or brown powder, of a bitter astringent taste, which is soluble in 800 parts of cold water, more easily in hot water. The solution is purple, and reddens litmus; it is turned yellow by acids. When heated, the powder explodes. The boiling solution gives to silk a deep purple colour; and, if different mordants be applied to the silk previously, it is dyed of all shades of brown, blue, violet, green, and yellow, according to the mordant. All these colours resist the action of soap; but are bleached, sooner or later, by the action of light.

According to Schunck, polychromic acid is a mixture of two acids, Aloetic and Aloeresinic acids. The latter forms with most bases brownish red insoluble salts. The aloetic acid, on the contrary, forms salts most of which are soluble. The aloetate of potash forms, when rapidly crystallized, small blood-red prisms; by spontaneous evaporation, long ruby-red needles. The composition of these acids is unknown.

Chrysammic Acid.—Formula, $C_{15}HN_2O_{12} + HO$. (Schunck.) One part of aloes and 8 of nitric acid, sp. gr. 1.37, are heated together, at first in an open vessel; and, when the first violent action is over, the whole is introduced into a retort, and distilled to two-thirds. More acid (about 4 parts) is then added, and the mixture kept at a heat near the boiling point for some days, as long as the gas is disengaged. The greater part of the acid being distilled off, water is added, which throws down impure chrysammic acid, while ehrysolepic and oxalic acids remain in solution.

The precipitated acid is purified by washing with water, which removes nitric, ehrysolepic, and aloetic acids. It then forms a greenish yellow crystalline powder, which still contains aloeresinic acid. It is now combined with potash, and the salt purified by recrystallization. The pure salt is dissolved in water; and, on the addition of nitric acid, pure chrysammic acid is deposited.

It forms a golden yellow powder, composed of shining scales, soluble to some degree in hot water, forming a purple solution, which is bitter. It is easily soluble in alcohol, ether, and hot acids; and when heated it explodes. When heated in fuming nitric acid, it is decomposed, yielding a new compound in golden scales, which forms with potash

an insoluble salt; with soda, one which crystallizes in needles of a greenish golden colour.

When heated with oil of vitriol, chrysammic acid yields dark grey adamantine crystals, which are a new compound. This substance, when its solution is mixed with nitric acid, yields shining yellow scales, which are not chrysammic acid.

Chrysammate of Potash forms, when crystallized out of a saturated boiling solution, a beautiful carmine-red crystalline powder; and, when more slowly produced, small greenish golden crystals, like those of murexide. The salts of soda and magnesia are similar.

With ammonia chrysammic acid forms a deep purple solution, which deposits dark green crystals. These are not chrysammate of ammonia, but probably an amide. If their solution be mixed with nitric acid, it becomes of a brighter colour, and on cooling deposits, not chrysammic acid, but black adamantine crystals, which, when boiled with potash, yield ammonia, and are reconverted into chrysammic acid.

The other salts of this acid are of various shades of red, and all exhibit a golden lustre under the polishing steel.

Chrysolepic Acid.—This acid is contained in the mother-liquid and washings of the preceding. It is obtained by evaporation in crystals, which are purified by being combined with potash, and the salt recrystallized. The solution of the pure salt, treated with nitric acid, yields pure chrysolepic acid, in beautiful golden-yellow scales, of a darker colour than picric acid, which, however, it resembles in its properties. According to Schunck, its formula is $C_{12}H_2N_3O_{13} + HO$, being the same as that of picric acid, from which it is distinguished by its salts. It is probable that these acids are essentially the same.

Chrysolepate of Potash forms long shining yellow needles, which exhibit a violet metallic lustre by reflected light. *Chrysolepate of Soda* forms long needles, which have a green metallic lustre. *Chrysolepate of Silver* forms dark brownish-red needles, which exhibit a play of red and green colours by reflected light.

A hot solution of the salt of potash or soda gives with acetate of lead yellow brilliant crystals, which are composed of basic chrysolepate and acetate of lead. These crystals dissolve in acetic acid; and the solution, when evaporated, deposits dark brown metallic-looking crystals, said to be neutral chrysolepate of potash. These characters serve to recognize the chrysolepic acid, and to prove that it differs from picric acid. The acid itself, and its salts, explode when heated, like picric acid and the picrates.

According to Boutin, when nitric acid and aloes are heated together in a retort, a volatile substance passes over, having the smell of bitter

almonds. Its properties are unknown, and Schunck could not observe its presence in his experiments.

Styphnic Acid.—By the action of nitric acid on gum ammoniac, assafoetida, and some other substances, Böttger and Will obtained this acid. It is very analogous to picric and chrysolepic acids, but contains 2 eq. of oxygen more.

ASPARAGINE.

Syn. Asparamide; Althéine; Agedoile.—Formula of the crystals, $C_8H_8N_2O_6 + 2HO$; when dried at 248° , $C_8H_8N_2O_6$. It occurs in asparagus, in liquorice, in the root of *Althæa officinalis*, in *Symphytum tuberosum*, in the potato, and probably in many other plants.

It is obtained either by macerating althæa-root with milk of lime, precipitating the filtered liquor with carbonate of ammonia, and evaporating to the consistence of syrup; or by boiling the juice of asparagus, filtering and evaporation. Piria has lately shewn that when vetches are made to grow in the dark, the juice of the etiolated plants contains a very large proportion of asparagine. He also states, that, when the juice is made to undergo fermentation, the asparagine is converted into succinic acid and ammonia. It forms large transparent right rhombic prisms, or short six-sided prisms, of a cooling somewhat nauseous taste. It is soluble in water and weak spirits, insoluble in alcohol and ether. By the action of acids and alkalies, aided by heat, it is resolved into ammonia and *aspartic acid*.

Aspartic Acid.—A bibasic acid. Formula of the hydrate, $C_8H_5NO_6 + 2HO$; of the anhydrous acid, $C_8H_5NO_6$.

Asparagine is boiled with aqua potassæ as long as ammonia is disengaged. The aspartate of potash is super-saturated with hydrochloric acid, and evaporated to dryness; cold water dissolves out the chloride of potassium, and leaves pure aspartic acid.

It forms delicate white micaceous scales of a pearly lustre, sparingly soluble in water, insoluble in strong alcohol. When boiled with strong potash, it is decomposed, yielding ammonia and a new acid, which is very soluble, but has not been studied.

It is derived from asparagine by the separation of 1 eq. ammonia, $C_8H_8M_2O_6 - NH_3 = C_8H_5NO_6$. The general formula of its salts is $C_8H_5NO_6 + 2MO$; but several exist of the formula $C_8H_5NO_6 + HO$, MO , as in other bibasic acids.

ORGANIC BASES OR ALKALIES.

The name of organic bases is applied, in the stricter sense, to a series of azotized compounds capable of forming salts with acids. They differ from the non-azotized bases, such as oxide of ethyle, oxide of methyle, &c., in this, that in their salts the acid may be transferred by double decomposition to other bases. In this respect the salts of the organic alkalies resemble those of ammonia.

Most of the organic bases are found ready formed in plants; these are called Vegetable bases. Others are formed in certain processes of decomposition. The name of Organic or Vegetable alkalies, or of Alkaloids, is given to those which in solution restore the blue of reddened litmus, or turn the yellow of turmeric to brown.

The first vegetable base was discovered by Sertuerner in 1804, and the number of them has very greatly increased since that time.

The first organic base, however, strictly speaking, known to chemists, was Urea, which occurs in the urine of most animals, and which was also one of the first examples of the artificial production of an organic compound. Of late years, a considerable number of basic compounds, closely analogous to the alkaloids, have been formed by artificial means, but, with the exception of urea, glycocoll, and kreatinine, none of these are identical with natural alkaloids. Urea has already been fully described; we shall, therefore, include in this section only those artificial organic bases which have not been previously mentioned. The whole subject of the alkaloids is one of great interest, but also of great difficulty; and as the artificial bases agree perfectly in all their general characters with the natural ones, it is of importance to study carefully the conditions under which the former are produced. It is only in this way that we can expect to be enabled hereafter to produce artificially such compounds as Quinine, Morphine, Strychnine, Veratrine, &c.; and the rapid progress of discovery in this department within the last year or two, encourages us to hope that this may one day be done.

In another point of view, the artificial formation of alkaloids is very interesting, namely, as throwing light on the constitution or intimate nature of this class of compounds. Hitherto, all attempts to ascertain, by direct experiment, the constitution of the vegetable bases, have failed; but the recent researches of Wöhler and of Blyth on narcotine have demonstrated that much may be done by studying the products of their decomposition. Berzelius also has lately been engaged in the investigation of the constitution of the alkaloids, although his results have not yet appeared. In the meantime, the researches

of Zinin, Laurent, Fownes, Hofmann, and of Liebig and Wöhler, have greatly extended the number of artificial organic bases, and added to our knowledge of the various methods in which they are formed; and, finally, the speculations of Fresenius, founded on these researches, have developed principles of arrangement and relations of composition, in this remarkable class of bodies, which will powerfully contribute to clear up the many obscure points in their chemical history.

We shall consider the alkaloids in two groups—the first containing the natural, and the second the artificial bases; and we shall conclude with some general views applicable to both.

I. NATURAL ALKALOIDS.

The general method of extracting them from the plant varies with the properties of the bases. When the base is insoluble in water, it is extracted by diluted acids, and the acid solution precipitated by an alkali. The same process applies where the insoluble base exists in the plant in the form of a soluble salt, which is extracted by water and decomposed by an alkali. The precipitated alkali is generally impure, and is purified either by crystallization from alcohol, or by converting it into a salt, which, when purified by recrystallization, yields the pure alkali on the addition of ammonia or some other base.

When the base is soluble, without being volatile, it is extracted by a dilute acid; and the concentrated solution is digested with potash and ether, which dissolves most or all of the vegetable bases of this class.

When it is soluble and volatile, the plant or its extract is distilled with potash, and yields a product containing the base with a mixture of ammonia. This is neutralized by oxalic or sulphuric acid, and evaporated to dryness. Alcohol now dissolves the sulphate or oxalate of the base, and this salt is agitated with potash and ether. The ether dissolves the base, and leaves it on being evaporated. The base is finally purified by distillation.

The alkaline character of the organic bases depends, in some way, on the nitrogen which they invariably contain. Many contain no oxygen; these are powerful bases: and, in contradistinction to the inorganic bases, those which contain oxygen neutralize less acid the more oxygen they contain. Most of them contain in 1 equivalent of the base 1 eq. of nitrogen; a few contain 2 or more equivalents of that element.

The organic bases, in the anhydrous state, combine directly with hydrogen acids.

Towards oxygen acids they behave like ammonia, combining only with the hydrated acids; and the hydratic water cannot be expelled from the salts without decomposition. Like ammonia, they form double salts with bichloride of platinum, when previously converted into hydrochlorates. They differ, however, from the ammoniacal salts in the amount of water of crystallization present in their compounds with hydrochloric acid.

The salts of Aconitine, Atropine, Brucine, Cinchonine, Codeine, Conicine, Delphinine, Emetine, Morphine, Narcotine, Quinine, Strychnine, and Veratrine, are precipitated white by infusion of galls. The precipitate is a tannate, which, when exposed to the air, passes into a soluble gallate.

When exposed to the action of chlorine, the vegetable bases are decomposed, yielding hydrochloric acid, which combines with the undecomposed residue of the base. In solutions of their salts, chlorine produces various effects. Thus, solutions of brucine become yellow, orange, red, blood-red, and at last yellow again. In a solution of a salt of strychnine chlorine causes a white precipitate, even when only $\frac{1}{800}$ th of strychnine is present. This precipitate contains chlorine and nitrogen. If brucine be present, it acquires a yellow or red colour. Solutions of cinchonine and quinine become yellow, rose-red, violet-red, and deposit a red resinous matter. Solutions of morphia become orange, blood-red, and lastly yellow, with a yellow precipitate. Narcotine becomes flesh-red, dark red, and finally deposits a brown powder. A solution of sulphate of quinine, saturated first with chlorine and then with ammonia, acquires a grass-green colour, and deposits a green powder.

When 2 parts of strychnine and 1 of iodine are dissolved in hot alcohol, there are deposited on cooling brilliant yellow scales, and the mother-liquor gives crystals of hydriodate of strychnine. From a solution of brucine in alcohol, tincture of iodine precipitates a brownish orange powder. Quinine and cinchonine, treated in the same way, yield clear brown liquids, which on evaporation first deposit saffron-coloured scales of a new compound, and lastly hydriodate of the base.

These new compounds seem to be composed of iodine and the base. With acids, iodine is set free, and the base remains dissolved. Their composition is not yet ascertained; and it is doubtful whether these compounds, described by Pelletier, are identical with those obtained by Bouchardat, by adding to the salts of organic bases a solution of ioduretted iodide of potassium.

When morphia is acted on by iodine, there are formed hydri-

odate of morphia and a brown compound which contains no morphia.

The action of acids on these bases is little known. Brucine and its salts are coloured red by nitric acid, also strychnine when it contains brucine. Morphia undergoes a similar change, and is also coloured brown by contact with a solution of iodic acid.

The action of alkalies on the organic bases has hardly been examined. According to Gerhardt, Quinine, Cinchonine, Strychnine, Narcotine, and some other bases, when heated with caustic potash, yield an oily liquid, which has alkaline properties. (See *Quinoline* or *Leucoleine*.)

In regard to the action of salts on the organic bases, we only know that morphia and its salts are coloured blue by the perchlorides of iron and gold. The blue colour is fugitive.

Such is a general account of this class of compounds. We shall consider them in the following order:—

1. Volatile bases, containing no oxygen;

These are Nicotine and Conicine.

2. Bases of Cinchona bark;

These are Quinine, Cinchonine, and Aricine (?).

3. Bases of the Papaveraceæ;

These are Morphia, Codeinc, Narcotine, Thebaine, Pseudomorphine, Narceine, and Chelidonine.

4. Bases found in the Solanaceæ, Strychnaceæ, and other plants;

These are Atropine, Solanine, Jervine, Brucine, Strychnine, Saba-dilline, Veratrine, Delphine, Staphisine, Menispermene, Picrotoxine, Emetine, Corydaline, Berberine, Piperine, Harmaline, Caffeine, and Theobromine.

It should be observed, that, although their alkaline characters depend on the nitrogen they contain, it appears, from all experiments hitherto made, that this nitrogen is not present in the form of ammonia.

It is also important to notice that the vegetable bases are either poisonous, or possessed of medicinal virtues; very commonly both. They are generally the active principles of the plants in which they occur.

The organic bases are often, for the sake of brevity, indicated, not by their formulæ, but by the initial letters of their names with the + sign over them. Thus, the abbreviated symbol of morphia is $\overset{+}{M}$.

1. VOLATILE BASES.

Nicotine. — Discovered in tobacco by Reimann and Posselt.

Formula, $C_{10}H_8N^+$. Symbol, N^+ . It is obtained by the general process above described for soluble and volatile bases. It forms a colourless clear oily liquid, which has a weak odour of tobacco, except when ammonia is present, in which case the smell is powerful. It boils at 585° , but is decomposed; it distils slowly, however, at a lower temperature. Its sp. gr. is 1.048. It has a distinct alkaline reaction, is miscible with water, and separates when the solution is saturated with hydrate of potash. It is very soluble in alcohol, ether, and oils. It is decomposed by exposure to air, and the action of chlorine, iodine, and nitric acid.

Nicotine is a frightful poison; one-fourth of a drop will kill a rabbit, one drop a dog. It does not dilate the pupil. It combines with and neutralizes acids, forming salts which are very soluble in water and alcohol, and crystallize with difficulty. Hydrochlorate of nicotine gives with bichloride of platinum a sparingly soluble and crystallizable double salt, which is slowly deposited in large orange-red prisms. If ammonia be present, the platinochloride of ammonium is instantly precipitated, and the filtered liquid on standing deposits the double salt of nicotine pure. Formula of this salt, $C_{10}H_8N, HCl + PtCl_2$.

A solution of nicotine in water gives with corrosive sublimate a white precipitate, the formula of which seems to be $2(C_{10}H_8N) + HgCl_2$. For the analysis, both of nicotine and of the two compounds just described, we are indebted to Ortigosa.

When nicotine is digested with fused potash, it yields two strata of liquid. The upper contains much potash, and, when distilled, yields an oily fluid of an agreeable odour, which forms with bichloride of platinum a very soluble salt in yellow scales, and is therefore distinct from nicotine.

Conicine. *Syn.* *Conia*; *Cicutine*. — Discovered by Gieseke, but first obtained pure by Geiger. Occurs in *Conium maculatum*. Formula, $C_{16}H_{16}N^+$ (?). (Ortigosa.) Symbol, Co^+ .

It is best obtained from the seeds by distillation with water and potash, and is purified in the manner recommended above for volatile bases. When pure, it forms a transparent colourless oily liquid, sp. gr. 0.89. It has a pungent and nauseous smell, which is stupefying and excites a flow of tears, and an acrid, pungent, nauseous taste. It is a most destructive poison, since from one-eighth of a grain to

one grain will destroy a small animal, death being preceded by rigid cramps. It does not enlarge the pupil. In the hydrated state it has a powerful alkaline reaction. It boils at 338° , but distils at a much lower temperature when water is present. It is partially decomposed when heated in contact with air, ammonia being produced. It is also decomposed by all the strong mineral acids, by chlorine and by iodine, yielding a great variety of colours, some of them beautiful.

Conicine is more soluble in cold than in hot water; and water also is more soluble in conicine when cold than when heated. It is easily miscible with alcohol and ether. It neutralizes acids completely, and its salts are very soluble, crystallizing with difficulty. Their solutions are easily decomposed, and the conicine gradually disappears, yielding ammonia and a bitter extractive matter which is not poisonous. The hydrochlorate forms *in vacuo* large foliated crystals which are deliquescent. Its solution, when evaporated in air, becomes first purple, then deep blue.

From the facility with which conicine is decomposed in the plant or its extract, the pharmaceutical preparations of hemlock are most uncertain in their activity. Hence pure conicine ought to be used, as it is uniform and may be preserved without difficulty.

2. BASES OF CINCHONA BARK.

Quinine. *Syn. Chinine.*—Formula, $C_{20}H_{12}NO_2$. (Liebig.) Symbol Q^+ . Discovered along with cinchonine, by Pelletier and Caventou. Occurs in all genuine cinchona bark, but in greatest abundance in *Cinchona regia vera*, or *Calisaya*, and in the yellow bark, *C. cordifolia*. The bark is exhausted, in an apparatus of displacement, by a dilute acid, the solution boiled with milk of lime, and the precipitate, when boiled with alcohol, yields quinine, generally mixed with cinchonine. The latter crystallizes readily, and the mother-liquor retains the quinine. Ether dissolves quinine from the dried residue, and leaves any cinchonine that may be present.

Quinine may be obtained in crystals from its solution in very strong alcohol by spontaneous evaporation, also from its solution in hot water with a little ammonia, in fine silky needles. It commonly occurs as a porous dirty white resinoid mass. The crystals are a hydrate. It is sparingly soluble in cold water, rather more so with the aid of heat, and the solution has an alkaline reaction. It is also soluble in alcohol and ether. Its solutions are bitter.

With acids it forms crystallizable salts, soluble in water and alcohol.

Solutions of these salts give with alkalis a flocculent white precipitate of quinine; and with tincture of galls a white precipitate. The most important of these salts is the sulphate, which is very extensively employed in medicine. Various processes are given for its preparation; but the essential part of all of them is to dissolve the impure quinine in dilute sulphuric acid, avoiding excess of acid, to digest the solution with animal charcoal, and to evaporate. The salt then forms fine light feathery crystals, which are snow-white. The sulphate of commerce is a basic salt, $2\overset{+}{Q} + SO_3 + 8HO$; and is preferred on account of its sparing solubility in cold water, which prevents material loss in its preparation. The neutral sulphate is much more soluble, and forms small needles. Other salts, such as the phosphate, acetate, hydrochlorate, citrate, ferrocyanate, kinate, &c., have been recommended for medical use. They are all very bitter to the taste.

The salts of quinine are often adulterated with gypsum, chalk, magnesia, boracic acid, sugar, mannite, starch, stearic acid, or salicine. Alcohol leaves the three first undissolved. If boracic acid be present, the alcohol will burn with a green flame. Sugar and mannite are extracted by cold water; and stearic acid is left undissolved by hot diluted acids. Starch is detected by iodine; and if salicine be the contamination, it is turned red by sulphuric acid. Salicine and cinchonine, however, if present, do not affect the medicinal virtue of the salts of quinine.

Gerhardt has recently shewn, (Ann. der Chem. und Phys. xlii. 310,) that, when quinine is distilled with potash and a little water, it yields an oily liquid, of basic properties, which he calls *Quinoline*, while hydrogen is given off.

This substance has since been shewn to be identical with *leucole* or *leucoline*, an oily base found in coal-tar, to be afterwards described.

Cinchonine is found in greatest abundance in the red bark (*C. oblongifolia*) and the pale bark (*C. condaminea*). In the former it is associated with much quinine; in the latter with very little or none. It is also found in yellow bark in smaller quantity than quinine. Formula, $C_{20}H_{12}\overset{+}{NO}$; symbol Ci.

The method of preparing it is the same as for quinine; and the alcoholic solution of the precipitate caused by alkalis deposits cinchonine in crystals by evaporation, while the quinine remains dissolved. Cinchonine forms large brilliant prisms, which may be volatilized by heat carefully applied. It is very insoluble in water, also in ether; soluble in strong alcohol.

It neutralizes acids, forming crystallizable salts, more soluble than

those of quinine and very bitter. Their solutions are precipitated white by alkalis and by tincture of galls. The sulphate may be employed for the same purposes as that of quinine.

It is to be observed, that the formulæ of quinine and cinchonine differ only by 1 atom of oxygen; and it is probable that one may be derived from the other, although this has not been proved experimentally.

Quinoidine.—This name has been given to a substance found in the mother-liquids of quinine and cinchonine, which has been described by several chemists as a new alkali. Liebig has lately shewn that it is quinine, in the amorphous or uncrystallizable state. Under the name of amorphous quinine, quinoidine is used as a cure for intermittents, and is said to be very effectual. It is given, like quinine, in the form of sulphate.

Aricine.—This name has been given by Pelletier to an alkali discovered by him in the *Cusco bark* or *Arica bark*. It is said to contain 1 atom of oxygen more than quinine; so that quinine, cinchonine, and aricine would be three oxides of the same radical. This, as well as the existence of aricine, requires confirmation. Nothing is known of its action on the system.

Several other alkalies are said to have been discovered in different varieties of cinchona bark, but their existence is doubtful.

3. BASES OF THE PAPAVERACEÆ.

Morphia or *Morphine*.—Formula, $C_{35}H_{20}NO_6$; symbol, M. ⁺Discovered by Sertuerner, 1804. The easiest method of preparing it is the following, proposed by Gregory and Robertson. An infusion of opium in cold water is concentrated, and heated with chloride of calcium in solution. The precipitate of meconate of lime, which separates, is removed by filtration, and the filtered liquid evaporated to the consistence of thin syrup. On standing, the liquid becomes nearly solid by the separation of hydrochlorate of morphia, which is purified by expressing the dark mother-liquor, and recrystallizing the salt, with the aid of animal charcoal. When the hydrochlorate is quite white, which may require from 2 to 4 crystallizations, according to the power of the press employed, it is dissolved in hot water, and supersaturated with ammonia, when the morphia falls as a snow-white, crystalline powder. (From the mother-liquid codeine is obtained.—See *Codeine*.) Many other processes have been given; but although some of them, in which alcohol is used, may answer well where that solvent is cheap, the above process, according to the experience of the Edinburgh manufacturers,

is the easiest and most productive, especially on a large scale. Good opium yields from 10 to 13 per cent. of morphia.

Merck precipitates the infusion of opium with carbonate of soda in excess, washes the precipitate with cold water and cold alcohol of sp. gr. 0·85, and dissolves the residue in weak acetic acid, from which, after filtering through charcoal, the morphia is precipitated by ammonia. It is finally crystallized from hot alcohol. This is an excellent process where alcohol is cheap.

Mohr adds the infusion to a milk of lime containing lime equal to one-fourth to one-sixth of the weight of the opium, boils for a short time, and filters while hot. The excess of lime dissolves the morphia, forming a wine-yellow solution, which is evaporated till it is double the weight of the opium, and then heated with powdered sal-ammoniac, one ounce being added for one pound of opium. On cooling, the morphia is deposited in coloured crystals, which are purified by a second solution in lime and precipitation by sal-ammoniac. This is also a good process, and is the best for operating on a small scale, as in testing the quality of opium.

Morphia forms, when crystallized from alcohol, brilliant colourless prisms, of adamantine lustre. The crystals contain 2 atoms of water, which are expelled by heat. It is fusible and is destroyed by a high temperature. Nitric acid colours it orange-red; iodic acid, brown, iodine being set free; and perchloride of iron, blue, which last colour is very fugitive.

It is very sparingly soluble in water; soluble in alcohol, especially with the aid of heat; insoluble in ether. Its alcoholic solution is very bitter. It likewise dissolves readily in the fixed alkalies and in lime. From the above characters, its purity is easily ascertained.

Morphia is the chief active principle of opium. In small doses it is powerfully anodyne; in large doses it causes death with narcotic symptoms. It is less active in the uncombined state than in the form of a salt, owing to its sparing solubility.

It neutralizes acids, forming crystallizable salts, of which the hydrochlorate, acetate, and sulphate are most employed. The preparation of the hydrochlorate has been described; but the commercial salt thus prepared generally contains about one-thirtieth of codeine. The pure hydrochlorate, as well as the acetate and sulphate, may be best prepared by dissolving pure morphia in the acids, and crystallizing. These salts form delicate feathery masses of fine crystals, similar to sulphate of quinine. They are generally sold in powder. Nitric and iodic acids and perchloride of iron act on them as on pure morphia. They are all easily soluble in alcohol. A solution of any of these salts, 5

grains to the ounce of water, forms an admirable substitute for laudanum, and is of the same strength. Ten grains of hydrochlorate of morphia have proved fatal; and probably half that quantity, or even less, would do so. It is very difficult to detect morphia or its salts after death, as they are rapidly removed from the stomach by absorption. Where opium or laudanum has been the cause of death, it is more easy to detect the meconic acid they contain, by its action on the salts of peroxide of iron.

Codeine.—Discovered by Robiquet in repeating the process of Gregory and Robertson above described. Formula, $C_{35}H_{20}^{+}NO_5$; symbol, Cd.

When the purified commercial hydrochlorate of morphia is precipitated by ammonia, the mother-liquor on evaporation yields a salt exactly like the hydrochlorate of morphia; but which is a double salt, composed of the hydrochlorates of morphia and codeine. It is digested with aqua potassæ, which dissolves the morphia, and leaves the codeine as an oily viscid mass, which, on cooling, consolidates into crystals. It is farther purified by ether, in which it dissolves; and by the addition of a little water, and spontaneous evaporation, it crystallizes in a state of purity.

Codeine is soluble in water, alcohol, and ether. Its aqueous solution deposits by slow evaporation very large transparent octahedrons. These, when heated, melt, and lose their water of crystallization. It has a bitter taste and is decidedly alkaline. It is not coloured by nitric acid, nor by perchloride of iron. It is insoluble in alkalies.

Codeine neutralizes acids and forms crystallizable salts, such as nitrate, sulphate, and hydrochlorate.

It seems to possess anodyne properties; and its salts often cause general and violent itching of the skin. (Gregory.) Perhaps codeine is the cause of the itching which often follows the use of opium and of the common hydrochlorate of morphia, which latter salt contains one-thirtieth of codeine. The pure hydrochlorate of morphia is said not to produce this effect. (Gregory.) As codeine is almost invariably present in opium, its action on the system deserves to be minutely investigated.

As an additional distinction of codeine from morphia, it may be added, that tincture of galls precipitates the salts of codeine abundantly, but does not act on those of morphia.

It is also to be remarked that the relation between the formulæ of codeine and morphia is the same as between those of cinchonine and quinine, the morphia containing 1 atom of oxygen more than the codeine.

Thebaine. *Syn. Paramorphine.*—Discovered by Thibouméry. Formula, $C_{25}H_{14}NO_3$. (Kane.)

When an infusion of opium is acted on by excess of lime, the morphia is dissolved; and the residuc yields, when dissolved in diluted acid and precipitated by ammonia, a powder, which, when, dissolved in alcohol or ether, leaves thebaine on evaporation.

It forms colourless crystals, has a sharp metallic taste, and an alkaline reaction. It is fusible. It combines with diluted acids, forming crystallizable salts. Its action on the system is unknown, and its formula is not ascertained with certainty.

Pseudomorphine.—Discovered by Pelletier, who, however, has only found it in two specimens of opium. Formula, $C_{27}H_{18}NO_{14}$?

It is sparingly soluble in water, insoluble in alcohol and ether, soluble in alkalies. It forms shining scales. It dissolves readily in acetic and hydrochloric acids, but its salts have not been studied. Like morphia, it is coloured blue by the salts of peroxide of iron.

Narceine.—Discovered by Pelletier. Occurs also in opium. Formula, $C_{28}H_{20}NO_{12}$? (Couerbe); or $C_{32}H_{24}NO_{16}$? (Pelletier). It is extracted from the brown mother-liquors of morphia or hydrochlorate of morphia by a tedious process. It is sparingly soluble in water, very soluble in alcohol, insoluble in ether, and may thus be purified from the other ingredients of opium. It forms fine silky crystals, which have a metallic taste. It dissolves in diluted acids without neutralizing them, and the solutions on evaporation deposit unaltered narceine. It is coloured blue by strong acids (yellow by nitric acid) and by substances having a strong attraction for water, such as chloride of calcium, but not by the salts of iron.

Narcotine.—Discovered by Derosne. Formula, $C_{46}H_{25}NO_{14}$.

Narcotine occurs also in opium, and is best obtained by extracting the residue, left by cold water, with acetic acid. The addition of ammonia causes a precipitate, which is dissolved in hot alcohol, decolorized by animal charcoal, and crystallizes on cooling.

It forms colourless shining needles, which are fusible. It is insoluble in water, soluble in alcohol and ether, insoluble in alkalies. Its solutions are very bitter. It is turned blue by the salts of peroxide of iron, and is not reddened by nitric acid; but sulphuric acid, containing a trace of nitric, tinges it blood-red.

It combines with acids, and some of its salts have been crystallized; but they have always an acid reaction. It is very doubtful whether narcotine or its salts, when free from morphia, &c., have any action on the system.

When, as often happens, morphia is contaminated with narcotine, it is separated, either by alkalies such as potash or lime, which dissolve the morphia and leave the narcotine, or by converting the mixture into a hydrochlorate and crystallizing. The whole of the narcotine remains in the mother-liquor.

The very recent researches of Liebig, Wöhler, and Blyth have made known a series of products of decomposition derived from narcotine, when acted on by peroxide of manganese and sulphuric acid, and also by bichloride of platinum. These our space will only permit us briefly to mention.

1. *Opianic Acid*.— $C_{20}H_9O_{10} = C_{20}H_8O_9,HO$. This acid crystallizes in slender prisms, and forms soluble and crystallizable salts with baryta and the oxides of lead and silver, and with oxide of ethyle. When melted, opianic acid passes into an insoluble state, its composition remaining the same.

2. *Opiammon*.— $C_{40}H_{17}NO_{16}$. This compound is derived from 2 eq. opianate of ammonia by the loss of 1 eq. ammonia and 4 eq. water. It is a pale yellow powder, which, by boiling with water, is converted into opianic acid and opianate of ammonia.

3. *Xanthopenic Acid*.—When opiammon is acted on by alkalies, it gives off ammonia and yields opianate and xanthopenate of potash. An acid separates the xanthopenic acid as a yellow flocculent precipitate. It forms salts of a fine yellow colour, but has not been fully examined. It contains nitrogen.

4. *Opiano-sulphurous Acid*.— $C_{20}H_8O_{11}S_2,HO$, is formed by the action of sulphurous acid on opianic acid, and is produced by the substitution of 2 eq. sulphurous acid for 2 eq. water. It has a bitter taste and forms crystallizable salts.

5. *Sulphopianic Acid*.— $C_{20}H_8\left\{\begin{smallmatrix} O_7 \\ S_2 \end{smallmatrix}\right\},HO$. This acid is formed by the action of sulphuretted hydrogen on opianic acid, and is, in fact, opianic acid, in which 2 eq. of oxygen are replaced by 2 eq. sulphur. It is an amorphous yellow powder, which crystallizes from alcohol. Its salts are soon decomposed, yielding sulphurets of the metal.

According to Wöhler, opianic acid is $(C_{20}H_6O_7,2HO) + HO$; and in the two preceding acids the 2 eq. of water represented within the brackets are replaced by 2 eq. sulphurous acid and 2 eq. sulphuretted hydrogen. Opiammon, on this view, is $(C_{20}H_6O_7,2HO) + (C_{20}H_6O_7, NH_3)$. He considers it probable that narcotine is a compound analogous to opiammon, and containing opianic acid.

6. *Hempinic Acid*.— $C_{10}H_4O_5,HO$. This is a product of oxidation of opianic acid. 1 eq. anhydrous opianic acid, $C_{20}H_8O_9$, plus

eq. oxygen, is $C_{20}H_8O_{10} = 2(C_{10}H_4O_5)$. The hempinic acid crystallizes in regular four-sided prisms. It forms insoluble salts with the oxides of lead and silver.

7. *Cotarnine*.— $C_{25}H_{13}NO_6$. This is a base formed along with opianic acid. 1 eq. narcotine ($C_{46}H_{25}NO_{14}$) and 7 eq. oxygen yield 1 eq. cotarnine ($C_{25}H_{13}NO_6$) + 1 eq. opianic acid ($C_{20}H_9O_{10}$) + 1 eq. carbonic acid (CO_2) + 3 eq. water, $3HO$.

Cotarnine forms a deep yellow radiated mass, soluble in alcohol and in water. It is bitter and alkaline, and forms crystallizable double salts with the bichlorides of mercury and platinum.

8. *Humopinic Acid* is a dark brown humus-like acid formed by the action of heat on narcotine. Its composition is not established with certainty, but resembles that of other similar bodies. It contains no nitrogen.

9. *Apophyllic Acid*.—This seems to be a product of decomposition of cotarnine. It forms crystals very like those of apophyllite and equally cleavable. When heated it yields an oily liquid, evidently quinoline. Its composition is not yet known, but it contains nitrogen.

10. *Narcogenine*, $C_{36}H_{19}NO_{10}$, is formed, along with opianic acid, when narcotine is not so far oxidized as to yield cotarnine. 2 eq. narcotine with 5 eq. oxygen yield 2 eq. narcogenine, 1 eq. opianic acid, and 3 eq. water. It forms a crystallizable double salt with bichloride of platinum, but, when separated, it is resolved into narcotine and cotarnine. 2 eq. narcogenine, with 2 eq. oxygen, contain the elements of 1 eq. narcotine, 1 eq. cotarnine, and 1 eq. carbonic acid.

11. *Narcotinic Acid*.—When narcotine is heated with potash it forms a soluble compound which contains an acid, apparently isomeric with narcotine, or differing from it only by 1 or 2 eq. water. When this acid, which is called narcotinic acid, is separated from its salts, it rapidly passes into narcotine, so that it is unknown in a separate form. Its atomic weight seems to be half that of narcotine, so that 1 eq. narcotine probably forms 2 eq. of the acid.

Such is a very brief and imperfect account of the results of the recent researches of Wöhler and of Blyth on narcotine. They are of very great importance as indicating a method which may lead to the discovery of the true constitution of the alkaloids.

Chelidonine.—Discovered by Godefroy; studied by Poxley, Probst, and Reuling. Occurs in *Chelidonium majus*, and in *Glaucium luteum*. Formula, $C_{40}H_{20}N_3O_6$. (Will.)

When pure it forms colourless scales, of a bitter taste, insoluble in water, soluble in alcohol and ether. It forms with acids crystallizable

salts, which have an acid reaction. Their action on the system has not been investigated.

From the same plants, *Chelidonium majus* and *Glaucium luteum*, Probst obtained another base, which he calls Chelerythrine. When pure it forms a grey powder, which powerfully excites sneezing. It is insoluble in water, soluble in alcohol. Acids give it a fine orange colour, and form with it coloured salts, which are neutral, and act as narcotics in a small dose. Some of these salts have been crystallized.

In *Glaucium luteum* Probst has, moreover, discovered two other bases, Glaucine and Glauopicrine. *Glaucine* forms pearly scales, which are soluble in hot water, in alcohol, and in ether. It is easily fusible; and forms with acids neutral salts, which are colourless, crystallizable, and have an acrid taste. When heated with oil of vitriol in an open vessel, it yields an indigo-blue product.

Glauopicrine forms white scales, soluble in hot water, ether, and alcohol. It has a bitter taste, neutralizes the acids perfectly, and forms colourless crystallizable salts, which have a bitter and nauseous taste. When heated with oil of vitriol it yields a dark green, tough mass.

4. BASES FOUND IN THE SOLANACEÆ, STRYCHNACEÆ, AND OTHER NATURAL FAMILIES.

Hyoscyamine.—Discovered by Geiger and Hesse in *Hyoscyamus niger*; occurs probably also in *H. albus*. Its formula is unknown.

It is purified by a tedious and difficult process, and much is lost in the various operations. It may be obtained in crystals, but is commonly got as a viscid mass. When moist it has a strong alkaline reaction, and a penetrating, narcotic, and stupifying odour, like that of nicotine. It is equally poisonous with nicotine, and produces the same symptoms, except that it enlarges the pupil strongly and permanently. It may be distilled, but is partially decomposed by heat; and it is rapidly destroyed by contact with alkalis. It is somewhat soluble in water, very soluble in alcohol and ether.

It neutralizes acids, forming salts, some of which crystallize, and all of which are poisonous. Hyoscyamine and its salts should be employed in medicine, as being more uniform in activity than the plant, or its extract, tincture, &c.

Daturine.—Discovered by Geiger and Hesse in *Datura stramonium*. It probably occurs in other species of *Datura*. Its formula is not yet ascertained.

It is best obtained from the seeds, by a method similar to that for hyoscyamine. It forms large brilliant prisms, in radiated groups. It

is sparingly soluble in cold water; more so in hot water, alcohol, and ether. When impure and moist, it has a nauseous narcotic odour. Its taste is at first bitter, then acrid; and it is as poisonous as hyoscyamine, dilating the pupil strongly. It may be sublimed unaltered, and is altogether less easily decomposed than hyoscyamine. Its solution in alcohol crystallizes with difficulty; but, if water be added, it yields fine prisms.

Daturine neutralizes acids and forms crystallizable salts, which have been little examined. Daturine and its salts deserve a trial as remedies.

Stramonine.—Found by Trommsdorff accompanying daturine. It crystallizes in needles, is insoluble in water, sparingly soluble in alcohol, very soluble in ether. It has neither taste nor smell; and may be sublimed, if cautiously heated. It is as yet little known.

Atropine.—Discovered by Mein, Geiger, and Hesse in *Atropa belladonna*. Formula, $C_{34}H_{23}NO_6$? (Liebig.) It is best obtained from the root, by a tedious process, analogous to those above described.

It crystallizes in small white prisms, which are soluble in water and alcohol. The solutions, when heated, are easily decomposed. It neutralizes acids, and forms salts, which are also easily decomposed, ammonia being one of the products.

It is a most energetic poison; and the smallest portion of it, or of any of its salts, produces great and permanent dilatation of the pupil. The extract of belladonna is much used in diseases of the eye; but is very variable in its activity, and sometimes inert. Atropine and its salts would, of course, if pure, be uniform in their effects.

Solanine occurs in several species of *Solanum*, and is found in considerable quantity in the shoots of potatoes which have germinated in a dark cellar. (Otto.) Formula, $C_{84}H_{68}NO_{28}$? (Blanchet.)

To obtain it the shoots are bruised, and extracted by water acidulated with sulphuric acid. The filtered solution is precipitated while hot with an excess of ammonia; and the precipitate, collected on a filter, washed with ammonia till the liquid passes through colourless, dried, and boiled with alcohol. The solution, filtered while hot, deposits on cooling a large quantity of pure solanine in light feathery crystals of a pearly lustre. (Otto; Reuling.)

Solanine is insoluble in water, soluble in hot alcohol. It neutralizes acids, forming crystallizable salts, which have an acrid taste. It is very poisonous. Its true formula is still doubtful.

Veratrine occurs in *Veratrum album* and *V. sabadilla*. Formula, $C_{34}H_{26}NO_6$? (Couverc.)

This alkali occurs in the form of a powder, which is hardly crystal-

line, and is probably not yet known in a state of purity. On this account its chemical history is very imperfect. It is insoluble in water, soluble in alcohol and acids, and has a very acrid taste. It is a powerful poison, and has been much employed as a remedy, chiefly externally, in tic-douloureux, rheumatism, sciatica, &c. Dr. Turnbull of London has used it with great success, and has published an account of his experiments. The powder applied to the nostril causes violent and dangerous sneezing.

Jervine.—Discovered by Simon in *Veratrum album* along with veratrine. Formula, $C_{60}H_{45}N_2O_5$. (Will.) It is white and crystalline, fusible, insoluble in water, soluble in alcohol. It forms with acetic acid a soluble salt; but, with sulphuric, nitric, and hydrochloric acid, salts which are very sparingly soluble in water. This property enables us to separate it from veratrine. Its action on the system is unknown.

Sabadilline.—Discovered by Couerbe in *Veratrum sabadilla*. Formula, $C_{20}H_{13}NO_5$? (Couerbe.) Of its chemical history and medicinal properties very little is known; and the formula above given, like that of veratrine, is doubtful.

Strychnine.—Discovered by Pelletier and Caventou in several species of *Strychnos*, such as *Strychnos nux vomica*, *S. colubrina*, and *S. Ignatii*. The latter contains most; but it is generally obtained from the more abundant *nux vomica*. Formula, $C_{44}H_{23}N_2O_4$; symbol, St.⁺

The process for preparing it is analogous to those for morphine and quinine. The alcoholic or aqueous extract is precipitated by lime, and the precipitate boiled with alcohol, which on cooling deposits impure strychnine. It is accompanied with brucine, which is separated by combining both with dilute nitric acid, and crystallizing. The nitrate of strychnine crystallizes readily, while that of brucine remains in the mother-liquid. From the pure nitrate the strychnine is precipitated by ammonia.

It forms a white powder, which requires about 7000 parts of cold water for solution, and gives to the water a most intense and persistent bitter taste. It dissolves in hot alcohol, sp. gr. 0.850, and on cooling is deposited in brilliant, colourless, transparent thick prisms or octohedrons. It is hardly soluble in absolute alcohol, and insoluble in ether. It is an energetic poison, acting on the nervous system, and producing tetanus. It is much employed as a remedy in paralysis, especially when partial.

Strychnine unites with acids, neutralizing them, and forming crystallizable salts. When pure, strychnine and its salts are not reddened by nitric acid; but when brucine is present, as in commercial strychnia, this effect is produced.

Brucine.—Discovered by Pelletier and Caventou in *Brucea antidysenterica*, and afterwards as accompanying strychnine in *Nux vomica*. Formula, $C_{44}H_{25}N_2O_7$. It would appear to be closely related to strychnine, containing 2 at. of water and 1 of oxygen more than that base, and therefore to bear to it the same relation as quinine to cinchonine or morphia to codeine.

Brucine neutralizes acids, forming crystallizable salts. It is soluble in water to a certain extent, very soluble in alcohol. It is strongly reddened by nitric acid. It has a very bitter taste; and its action on the system is the same as that of strychnine, only much less energetic. Hence the presence of a little brucine in the strychnine of commerce is not injurious.

Delphine occurs in *Delphinium Staphysagria*. Formula, $C_{27}H_{19}NO_2$? (Coucherbe.) It is obtained as a powder analogous in its characters to veratrine, and has been employed with almost equal success by Dr. Turnbull.

Staphysine accompanies delphine. Formula, $C_{32}H_{23}NO_2$? (Coucherbe.)

Aconitine.—Discovered by Geiger and Hesse in *Aconitum napellus* and *A. ferox*. Our knowledge of this base is very limited. There is reason to think, from the experiments of Dr. Turnbull, either that the plant contains two bases, or that the aconitine of Geiger and Hesse is an altered product. Dr. Turnbull has succeeded in producing, but with difficulty and in small quantity, an aconitine possessing in perfection all the active properties of the plant. It produces numbness of the tongue when applied to it, and is said to contract the pupil, whereas Geiger's aconitine dilates it. In obtaining the aconitine of Turnbull much appears to depend on the freshness of the plant; and the alkaloid itself is easily decomposed, especially by alkalies.

As a remedy in neuralgia and similar painful and obscure diseases, the aconitine of Turnbull possesses most valuable powers. Could it be obtained at a reasonable price, it would be extensively employed. At present, however, only one manufacturer has been able to obtain it, and that in small quantity. The aconitine of Geiger and Hesse does not appear to possess the same action on the system.

Bebeerine is the active principle of the Bebeeru tree of Guiana. It has not been obtained in crystals, but as a brown transparent mass, the composition of which MacLagan and Tilley found to be the same as that of morphia. Its sulphate is a good deal used as a substitute for sulphate of quinine.

Picrotoxine.—Discovered by Boullay in *Cocculus indicus*, the

seeds of *Menispermum cocculus*; and examined by Pelletier, Couerbe, and Regnault. These chemists stated that it contained no nitrogen; but the recent researches of Francis have shewn that, like other vegetable bases, it is azotized. Its true formula has not yet been published by the latter chemist, but he found in it 1.38 per cent. of nitrogen.

It forms colourless prisms, which have an intensely bitter taste. It is soluble in hot water and in alcohol. Its basic properties appear to be feeble. It is very poisonous.

Menispermine.—Discovered by Pelletier and Couerbe in *Cocculus indicus*. Formula, $C_{18}H_{12}NO_2$?

Paramenispermine.—Said by the same chemists to accompany the preceding, and to have the same composition, but different properties.

Emetine is the emetic principle of *Cephaelis ipecacuanha*. It is a white powder, slightly bitter, fusible, sparingly soluble in water, very soluble in alcohol. Formula, $C_{37}H_{27}NO_{10}$? (Pelletier.)

Harmaline.—Discovered by Göbel in the seeds of *Peganum harmala*. Formula, $C_{24}H_{13}N_2O$. (Varrentrapp and Will.)

It forms yellowish brown crystals, of a bitter astringent and acid taste, sparingly soluble in water and ether, more soluble in alcohol.

It is basic, and forms with acids yellow soluble salts, some of which crystallize. Harmaline may be used as a yellow dye; and by oxidation may be made to yield a magnificent red dye-stuff, which is likely to be much employed, as the seeds are produced abundantly in southern Russia, and the preparation and application of the colouring matter, according to Göbel, are very easy. Fritzsche has observed that harmaline is converted by oxidation in different ways into two new bases, one white (*leucoharmine*), the other yellow (*chrysoharmine*). Their composition is not given.

Piperine occurs in both white and black pepper. Formula, $C_{34}H_{19}NO_6$. (Regnault.) It is commonly considered as neutral; but, according to Varrentrapp and Will, it combines, like the vegetable alkalies, with hydrochloric acid gas, forming a salt which unites with bichloride of platinum. The hydrochlorate of piperine is decomposed by water.

Piperine forms rhomboidal prisms, which are colourless, tasteless, and inodorous; fusible, not volatile. It is nearly insoluble in water, soluble in alcohol, and with oil of vitriol gives a red colour.

Berberine.—Discovered by Buchner in *Berberis vulgaris*. Formula, $C_{33}H_{18}NO_{12}$. It forms a bright yellow crystalline powder, of a silky lustre, which has a strong bitter taste. It is sparingly soluble in

cold water, but tinges it strongly yellow. It dissolves more easily in boiling water and alcohol, and is deposited in crystals on cooling. It is insoluble in ether.

It is decomposed by strong acids, and sparingly dissolved by dilute acids. Alkalies colour it brown, and it combines with several metallic oxides. It forms an insoluble compound with tannic acid. Its basic characters are very indistinct, and it would rather appear to belong to the class of azotized colouring matters.

Corydaline occurs in the root of *Corydalis bulbosa*, and *C. fabacea*. Formula, $C_{34}H_{22}NO_{10\frac{1}{2}}$? (F. Dœbereiner.)

Caffeine. *Syn. Theine; Guaranine*.—Discovered by Pfaff in coffee. Occurs also in tea (*Thea viridis* or *T. bohea*), and in *Guarana officinalis*, and in *Ilex paraguayensis*. Caffeine, theine, and guaranine, at first described as distinct compounds, have recently been proved to be identical. Formula, $C_8H_5N_2O_2$. (Pfaff and Liebig; Jobst; Martius.)

Caffeine forms silky white needles, sparingly soluble in cold water and alcohol, easily with the aid of heat. It crystallizes readily from an infusion of raw coffee, when certain impurities have been removed by subacetate of lead, and the excess of lead by sulphuretted hydrogen. It has a mild bitter taste.

With sulphuric and hydrochloric acids it forms crystallizable compounds. The latter yields large and beautiful crystals.

Although caffeine has no poisonous properties, and does not exhibit a marked action on the system, it is highly probable that it produces important effects. In addition to the remarkable fact, that it is found in tea and coffee, in guarana and in the Paraguay tea, all of which are used by whole nations as a refreshment, Liebig, in his late work on Animal Chemistry and Physiology, has shewn that the composition of caffeine is closely related to that of various animal products; and that there is reason to believe that it may assist in the production of bile, and thus facilitate the process of respiration.

Theobromine.—Discovered by Woskresensky in the seed of *Theobroma cacao*, which yields chocolate and cocoa. Formula, $C_9H_5N_3O_2$, or $C_{18}H_{10}N_6O_4$.

It is very similar to caffeine, having the same taste; but is almost insoluble in water, alcohol, and ether. It is remarkable for the large proportion of nitrogen it contains, about 35.4 per cent.

It not only occurs in a substance which is used with the same intention as tea and coffee, for the sake, namely of its power in refreshing and gently stimulating the system; but has also been shewn by Liebig to be closely related, as caffeine is, to urea and uric acid. This renders the opinion still more probable, that caffeine and theobromine contribute

to the formation of bile, with which that of urine is connected, and thus aid the process of respiration.

A number of substances have been named and described as vegetable alkalies, the true history of which is so little known that it is at present unnecessary even to give a list of them. Many are probably neutral, and identical with some of the neutral vegetable products formerly described. Others will perhaps be found to be identical with known alkalies. In all cases, further experiments are wanting.

II. ARTIFICIAL ALKALOIDS.

This section includes those alkaloids which are only known as products of chemical change. Some of the natural organic bases have also been formed artificially, as, for example, urea and kreatinine; and several of the artificial bases have already been described under other heads, as melamine, ammeline, the bases containing platinum, the bases derived from narcotine, and those derived from oil of bitter almonds, amarine, lophine, and picrine. We shall now briefly describe the remainder.

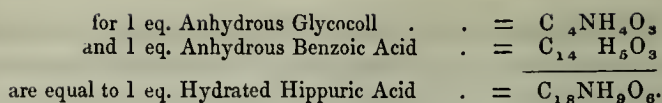
The artificial alkaloids are formed in several different ways. As, however, they all contain nitrogen, if we except the oxide of kakodyle and the oxide of kakoplatyle, ammonia is generally directly or indirectly concerned in their formation. Artificial urea is produced by a spontaneous metamorphosis of the cyanate of ammonia; melamine and ammeline, by the action of potash on sulphocyanide of ammonium; sinnamine and the allied bases, by the action of ammonia on oil of mustard; amarine, picrine, and lophine, by the action of ammonia on the oil of bitter almonds and its derivatives; furfurine, by the action of ammonia on furfurole; and thialdine and selenaldine from aldehydammonia by means of sulphuretted and seleniuretted hydrogen. Naphthalidine, seminaphthalidine, aniline, and toluidine are obtained by the action of sulphuret of ammonium on nitronaphthalase, nitronaphthalese, nitrobenzide, and nitrotoluide. But some alkaloids are formed without the aid of ammonia. Thus, sarcosine and kreatinine are obtained by the action of bases and of acids on kreatine; glycocoll, by the action of acids on hippuric acid, or of potash on gelatine; aniline, picoline, and leucoline, by the destructive distillation of nitrogenized compounds, in which latter case, however, ammonia may probably act; and aniline, chloraniline, bromaniline, with some other allied compounds, are obtained by the action of potash at a high temperature on isatine, chlorisatine, bromisatine, and their congeners. It is probable that other methods of producing basic compounds will be discovered: in the

meantime, it is interesting to observe that the known methods are chiefly processes of reduction or deoxidation; insomuch that several of these artificial alkaloids are destitute of oxygen, and in all the proportion of oxygen is small, as it is in the natural alkaloids.

It is also worthy of notice that these processes of reduction appear at the same time, in many cases, to act in causing the molecules of compounds of small atomic weight to coalesce, so as to produce more complex molecules. Until a very recent period all the organic compounds artificially formed by chemistry were less complex than those from which they were obtained; and they were chiefly produced by processes of oxidation; while the reducing agencies, as applied to organic compounds, and the power of building up, as it were, complex molecules from more simple ones, were confined to the living vegetable kingdom. It is obvious, therefore, that the discovery of means by which these two objects may be attained, and artificial compounds, entirely analagous to the natural ones, may be formed, must shed much light on the true nature of the processes going on in living plants and animals. It is chiefly in this point of view, and as bearing on physiology, that the artificial alkaloids, a class of bodies almost entirely of very recent discovery, and the number of which is rapidly increasing, are interesting to the philosophical chemist. They likewise afford some interesting examples of the law of substitution.

We shall now describe the artificial alkaloids in the order of their atomic weights; deviating, however, from this arrangement, in order to describe together those derived from a common source.

Glycocoll. Syn. Sugar of Gelatine.—This compound was first obtained as a product of the decomposition of gelatine by boiling with potash; but Dessaignes has lately shewn that it is much better prepared by the action of strong acids on hippuric acid. When this acid is boiled with an excess of strong hydrochloric acid, it is entirely decomposed, being resolved into benzoic acid and glycocoll. When the decomposition is complete water is added, the whole is boiled, and on cooling the greater part of the benzoic acid crystallizes. The liquid is evaporated to dryness in the water-bath, and when the residue has been dissolved and again dried up, the benzoic acid which was left at first is found to have been dissipated with the vapours. The residue is nearly pure hydrochlorate of glycocoll. It is now dissolved in a very small quantity of water, supersaturated with ammonia, and absolute alcohol added in excess, which causes a crystalline deposit of pure glycocoll. It may be obtained in large crystals by the spontaneous evaporation of its aqueous solution. Its formula is $C_4NH_5O_4 = C_4NH_4O_3 + HO$. Its production is easily explained,



Glycocoll has a strong sweet taste, and is soluble in water; insoluble, or nearly so, in alcohol and ether. It is placed in this section because it forms crystallizable salts with acids; but Horsford has shewn that it has a remarkable tendency to form crystallizable compounds with almost every class of compounds, with bases, with neutral salts, as well as with acids. Its composition is such, that it is, or may be, closely related to a number of very different compounds. Thus, 1 eq. of anhydrous glycocoll contains the elements of fumaric acid and ammonia; or of cyanate of oxide of methyle; or of succinic acid, amide, and water: 2 eq. of glycocoll contain the elements of asparagine; or of urea and $\frac{1}{2}$ eq. of grape sugar; or of allophanate of oxide of ethyle; and hydrated glycocoll has the same composition as hyponitrite of oxide of ethyle. As Horsford remarks, a compound of this kind may be expected to exhibit a great variety of characters, and it is difficult to fix its place. But, as its basic characters are tolerably well marked, it is here mentioned. The fact that it occurs as a product of decomposition of various animal substances, and that substances closely related to it, such as hippuric acid, asparagine, fumaric acid, &c., are found in animals and vegetables, render it highly probable that glycocoll will hereafter be found to play an important part in living organisms.

The salts of glycocoll form large and very beautiful crystals, and its compounds generally have a strong tendency to crystallize; but, for details, we must refer the reader to Horsford's able monograph in the *Annalen de Chemie und Pharmacie*, vol. lx. p. 1.

Sarcosine.—This base has recently been discovered by Liebig, as a product of the action of bases on *kreatine*, a crystalline compound occurring in the juice of muscle or flesh, to be afterwards described.

When *kreatine* is boiled with a large excess of hydrate of baryta, it is gradually decomposed, ammonia being disengaged, and carbonate of baryta deposited. The filtered liquid, after the excess of baryta has been removed by a current of carbonic acid gas, yields, on evaporation, *sarcosine*, which is purified by converting it into sulphate, which is then decomposed by digestion with carbonate of baryta. The solution of *sarcosine*, evaporated to a syrup, and then set aside for two days, deposits the base in crystals.

Sarcosine forms right rhombic prisms, very soluble in water, sparingly in alcohol, insoluble in ether. By a heat of 212° it is not altered; at a somewhat higher temperature it melts, and may be sublimed with-

out residue. It is even slowly volatilized at 212° . Its composition is represented by the formula $C_6NH_7O_4$; and its production from kreatine is thus easily understood. Kreatine (hydrated) is $C_8N_3H_{11}O_6$; and if we subtract from this formula that of sarcosine, the remainder, $C_2N_2H_4O_2$, is the formula of urea. Liebig has proved that urea is separated from kreatine in this process; but it is gradually converted into carbonic acid and ammonia by the action of the baryta and water at the boiling point.

Sarcosine does not alter vegetable colours, but it combines with and neutralizes acids, forming salts. Liebig has analyzed and described the hydrochlorate, the sulphate, and the double salt, formed by the hydrochlorate with bichloride of platinum. The characters of these salts correspond with those of the salts of organic bases in general.

It is worthy of remark, that sarcosine is isomeric with *lactamide* and with *urethane*, (see those substances,) from both of which, however, it is easily distinguished, not only by its basic characters, but by its insolubility in ether, and its sparing solubility in alcohol. Liebig obtained, however, in the process of preparing it, a small quantity of a different substance, resembling urethane, so that this latter compound may also be a product of the reaction.

Sarcosine has been as yet, for want of time and material, but imperfectly studied. It possesses considerable interest on account of its origin; and it is very probable that it may hereafter be found in the organism, as kreatine and urea are, the former the substance which yields it, the latter the product accompanying its formation.

Kreatinine.—This base occurs in the organism, and should, therefore, have a place in the list of natural bases; but when that section was written, it was only known as a product of the action of acids on kreatine.

In 1844 Pettenkofer discovered in urine a new compound, possessing the singular character of forming a crystalline compound with chloride of zinc, to which, however, he gave no name. The analysis of the purified organic matter, after separating the chloride of zinc, yielded the formula $C_8N_3H_8O_3$. In his very recent researches on flesh Liebig found that kreatine, $C_8N_3H_{11}O_6$, when heated with acids, lost 4 eq. of water, and was thereby transformed into a powerful base, which he called kreatinine, and the formula of which is, of course, $C_8N_3H_7O_2$. This only differs by 1 eq. of water from the formula of Pettenkofer's compound; and Liebig, suspecting their identity, examined the latter, and found that it was separated by alcohol into a more soluble and a less soluble compound. These he analyzed, and found that the more

soluble substance was in every respect identical with kreatinine, the less soluble with kreatine. He further shewed that kreatinine exists ready-formed along with kreatine in the juice of flesh.

To obtain both these compounds from human urine, Liebig recommends to neutralize morning urine with lime water, adding chloride of calcium, so as to precipitate all the phosphoric acid, to evaporate to a thin syrup the filtered liquid, and after removing the salts which crystallize out, to add to every pound of the concentrated liquid about $\frac{1}{2}$ oz. of a pure and saturated solution of chloride of zinc. On standing, the mixture slowly deposits, in crusts, and small spherical hard masses, a yellowish crystalline compound, which, according to Liebig, is essentially a compound of chloride of zinc with kreatinine, mixed with crystals of uncombined kreatine in variable quantity. It is washed with cold water, in which it is very sparingly soluble, and then dissolved in boiling water, and the solution boiled for half an hour with a great excess of hydrated oxide of lead, by which means the whole of the zinc and of the chlorine are separated in an insoluble form, as oxide of zinc and basic oxychloride of lead. The filtered liquid is boiled with a little blood charcoal, to remove colouring matter and a trace of oxide of lead, and then dried up in the water bath. The residue consists of kreatine and kreatinine, which are separated by boiling them with 8 or 10 parts of alcohol. If any part is left undissolved it is kreatine, and the crystals deposited on cooling are likewise kreatine. The liquid filtered from them contains the kreatinine. When the juice of flesh has been treated as will be afterwards described, for the purpose of obtaining kreatine, the mother-liquid, acted on by chloride of zinc, yields a crystalline precipitate identical with that from urine, from which, of course, kreatinine and kreatine may be extracted.

To prepare kreatinine from kreatine, Liebig directs to evaporate it to dryness with an excess of strong hydrochloric acid. The residue is hydrochlorate of kreatinine, from which, by boiling it with an excess of hydrated oxide of lead, the base is readily obtained. If sulphuric acid be used to act on the kreatine, (for 1 part of kreatine, 1 part of an acid composed of 27 of oil of vitriol, and 73 of water,) sulphate of kreatinine is obtained, and this is decomposed by adding carbonate of baryta to the boiling solution of the salt as long as effervescence ensues.

In either case the solution of kreatinine yields on evaporation well-formed crystals of the base. Kreatinine forms prismatic crystals, which dissolve in 11.5 parts of water at 60°, and in about 100 of alcohol at the same temperature. Its solutions act strongly both on litmus and turmeric paper, and in its chemical relations it is very analogous to ammonia. It forms with nitrate of silver a crystalline basic compound,

and with corrosive sublimate a curdy precipitate, soon changing into crystals of a nature analogous to white precipitate. With chloride of zinc it forms the crystalline compound formerly mentioned, and, when added to salts of copper, gives rise to crystallizable double salts of a fine blue colour. With bichloride of platinum hydrochlorate of kreatinine forms a double salt, which yields large aurora-red crystals. Kreatinine is a very powerful base, and expels ammonia from its salts.

The formula of kreatinine is $C_8N_3H_7O_2$, which differs from that of kreatine by 4 eq. of water. The very accurate analysis by Pettenkofer of his compound from urine gave the formula $C_8N_3H_8O_3$; but, as Liebig has shewn that it was really a mixture of kreatinine and kreatine, the apparent discrepancy, amounting to 1 eq. of water, is accounted for. A mixture of 1 eq. of kreatine with 3 eq. of kreatinine has exactly the composition found by Pettenkofer.

When urine undergoes putrefaction, the kreatine disappears, but the kreatinine remains unchanged. When putrid urine, therefore, is boiled with lime till all ammonia is expelled, concentrated, filtered, and mixed with chloride of zinc, crystals of the compound of the chloride of zinc with kreatinine are obtained.

Kreatinine is a substance, the occurrence of which both in the juice of flesh and in urine gives it considerable interest, especially when we consider its great basic energy. If we could ascertain with certainty the function it performs in the organism, we should certainly, as Liebig remarks, approach more nearly to the theory of the action of alkaloids on the system. For details in regard to this and the preceding base, as well as for the minute history of kreatine and the other ingredients of flesh, the reader is referred to Baron Liebig's latest work, entitled "*Researches on the Chemistry of Food.*"*

BASES FROM OIL OF MUSTARD.

Thiosinamine.—When the oil of mustard is brought in contact with three or four times its volume of strong ammonia, crystals are formed, which are purified by recrystallization. These are Thiosinamine. Formula, $C_8H_8N_2S_2$. (Varrentrapp and Will.)

Thiosinamine is soluble in hot water, less so in cold water, soluble in alcohol and ether. It has a bitter taste and no smell. At 392° it is resolved into ammonia and a resinoid basic compound not fully investigated. Thiosinamine combines with acids, but its salts do not crystallize: it yields a double salt with chloride of platinum,

* London, 1847. Taylor and Walton.

$C_8H_8N_2S_2, HCl + PtCl_2$; and a compound with corrosive sublimate, which is $C_4H_4NS + HgCl_2$.

Sinnamine.—Obtained by digesting thiosinnamine with moist hydrated protoxide of lead till all the sulphur is removed. The mass is then extracted by water, finally by alcohol, and the liquors evaporated to a syrup, which after some time deposits fine transparent crystals of sinnamine.

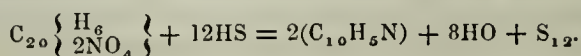
Sinnamine is a powerful base, expels ammonia from its salts, and precipitates the solutions of peroxide of iron, of copper, and of lead. It combines with acids, but yields no crystallizable salts. It precipitates the bichlorides of platinum and mercury, and nitrate of silver. When heated, it gives off ammonia, and leaves a resinoid mass which is also basic. The production of sinnamine from thiosinnamine is easily explained, as it is formed by the separation of all the sulphur and an equivalent amount of hydrogen. Thus, $C_8H_8N_2S_2 + 2PbO = C_8H_6N_2 + 2PbS + 2HO$. It is not known with certainty whether the formula of sinnamine is $C_8H_6N_2$ or C_4H_3N . (Varrentrapp and Will.)

Sinapoline.—This compound, discovered by Simon, is obtained by depriving oil of mustard of its sulphur by the action of baryta or of oxide of lead. It is soluble in hot water and alcohol, and crystallizes in shining, fatty, fusible scales. Its solution has an alkaline reaction. It combines with acids, and is separated from them by ammonia. It also precipitates, when combined with hydrochloric acid, the bichlorides of platinum and mercury.

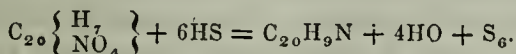
It is formed from oil of mustard by the subtraction of 2 at. of bisulphuret of carbon, and the addition of 2 at. of water. Thus, $C_{16}H_{10}N_2S_4 + 2HO = C_{14}H_{12}N_2O_2 + 2CS_2$. Formula of sinapoline, $C_{14}H_{12}N_2O_2$.

BASES DERIVED FROM NAPHTHALINE.

Seminaphthalidine.—This base, discovered by Zinin, is formed when an alcoholic solution of nitronaphthalène is acted on by sulphuret of ammonium. It forms reddish-yellow prisms, of metallic lustre, insoluble in water, soluble in alcohol and ether, and yielding crystallizable salts with acids. In its formation, nitronaphthalène, $C_{20}\left\{\begin{smallmatrix} H_6 \\ 2NO_4 \end{smallmatrix}\right\}$, loses all its oxygen, and is resolved, with the addition of hydrogen derived from the sulphuretted hydrogen, into 2 eq. of the new base, the formula of which is $C_{10}H_5N$.



Naphthalidine.—When nitronaphthalase, $C_{20}\left\{\begin{smallmatrix} H_7 \\ NO_4 \end{smallmatrix}\right\}$, is acted on by sulphuret of ammonium, there is formed, according to Zinin, a new base, naphthalidine, the formula of which is $C_{20}H_9N$.



Naphthalidine has all the characters of an organic base; it forms colourless crystals, soluble in alcohol and ether, and combines with acids, yielding crystallizable salts.

BASES OCCURRING IN COAL TAR.

Aniline. Syn. Crystalline; Benzidam; Kyanole.—Formula, $C_{12}H_7N$.

This remarkable compound was first discovered by Unverdorben among the products of the distillation of indigo, and called by him *crystalline*, from its marked tendency to form crystallizable salts. Runge afterwards described a similar compound in coal tar, to which he gave the name of *kyanole*, from its striking a deep blue with bleaching liquor. Fritzsche described it under the name of *aniline*, as a product of the action of heat on anthranilic acid, (see that substance;) and, lastly, Zinin obtained it by the action of sulphuret of ammonium on nitrobenzole, (nitrobenzide,) and named it *benzidam*. A. W. Hofmann, in his elaborate investigation of the bases in coal tar, shewed the identity of the substance described under these different names, and has subsequently shewn that it may be obtained by heating isatine with potash, and by a great variety of processes from a number of different compounds, so that it now appears as a very frequent product of the decomposition of nitrogenized substances. The same chemist has greatly extended our knowledge of aniline and of its derivatives.

From the oil of coal tar, when it can be procured, aniline is obtained by acting on it with hydrochloric acid, which extracts the basic oils. The solution is neutralized by an alkali, and the oil which separates is subjected to rectification. The aniline is found in that portion which distils near to its boiling point, 360° ; and, when repeatedly rectified, that which passes over at 360° is nearly pure. It is finally purified by converting it into oxalate, and distilling this salt, after several crystallizations, with potash.

Aniline is an oily liquid, colourless, and of a very high refractive and dispersive power. Its sp. gr. is 1.020. It has a burning aromatic taste, and an agreeable vinous smell. It boils at 360° , and is not congealed by a cold of -4° . It evaporates at all temperatures, and when

exposed to the air turns brown. It does not act on litmus or turmeric, but turns to green the colouring matter of the *dahlia*. A drop of it, placed on fir wood, and moistened with hydrochloric acid, strikes a deep yellow colour. It neutralizes acids, and forms, with all that have been tried, salts which crystallize with remarkable facility. When exposed to air, the salts of aniline generally acquire a rose-colour, gradually passing into brown. Our space does not admit of a detailed account of these salts, for which the reader is referred to Dr. Hofmann's paper, *Ann. der Ch. und Ph.*, xlvii. p. 37.

Aniline is readily recognized by its power of forming, with a solution of bleaching-powder, a compound of a deep but fugitive blue, or rather purple colour. The same blue compound is formed when hypochlorous acid (chlorous acid of Millon) is added to a solution of hydrochlorate of aniline. It is a product of oxidation, but, according to Fritzsche, contains also chlorine. Its composition, however, is still unascertained. By the action of a mixture of chlorate of potash and hydrochloric acid, aniline is finally resolved into chloranile and ammonia, accompanied by chlorophrenusic acid. Nitric acid converts it into picric (nitropicric or nitrophenisic) acid. Chlorine converts aniline into chlorophenisic (chlorindoptenic) acid and trichloraniline (chlorindatmit). Bromine gives rise to the formation of tribromaniline (bromaniloid). All these transformations indicate that aniline belongs to the series of phenyle, which, as we have already seen, includes many of the derivatives of indigo, as well as of salicine, along with numerous products of the destructive distillation.

The following table will illustrate the relation of aniline and its derivatives to the hydrate of phenyle:—

Hypothetical Radical	. . . $C_{12}H_5$	. . . Phenyle.
Carbolic Acid	. . . $C_{12}H_5O,HO$	. . . Hydrated oxide of Phenyle.
Chlorindoptenic Acid	. . . $C_{12}\left\{\begin{smallmatrix} H_2 \\ Cl_3 \end{smallmatrix}\right\}O,HO$	. . . Chlorophenisic Acid.
Chlorinized Chlorindoptenic Acid	$C_{12}Cl_5O,HO$	. . . Chlorophenusic Acid.
Nitropicric, or Picric Acid	. . . $C_{12}\left\{\begin{smallmatrix} H_2 \\ 3NO_4 \end{smallmatrix}\right\}O,HO$	. . . Nitrophenisic Acid.
Aniline, $C_{12}H_7N$	. . . = $C_{12}H_5 + \bar{N}H_2$	. . . Phenylamide, or Amaphenase.

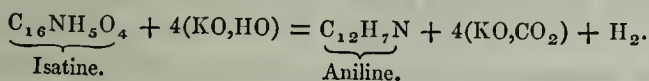
In this view, aniline is composed of phenyle and amide; and, whether this be so, or not, it is certain that every one of the compounds in the above table may be converted into chloranile by the action of chlorate of potash and hydrochloric acid, which, taken along with their common origin in indigo, would indicate a close relation among them all.

Perhaps no basic organic compound has been formed in so many different ways as aniline, and it is important to attend to this, because some or all of these methods may be hereafter employed to produce other bases.

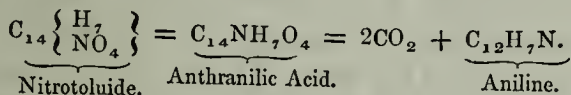
1. It is formed in the destructive distillation of coal and of indigo. As anthranilic acid, when heated, is resolved into aniline and carbonic acid, it is possible that in the case of indigo anthranilic acid is first formed and then decomposed. The decomposition of anthranilic acid is very simple.



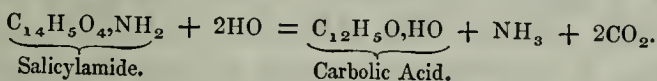
2. It is obtained when isatine is heated with potash, or when nitrotoluide is heated with lime. In the former case the change is as follows:—



In the latter case, nitrotoluide being isomeric with anthranilic acid, the explanation above given applies, the lime being omitted.

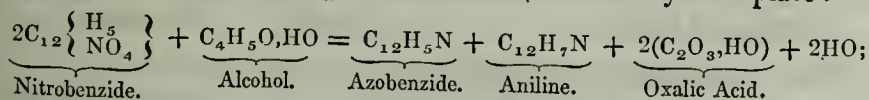


There is another compound, also isomeric with anthranilic acid, namely, *salicylamide*. But when this is heated, with or without a base, it is converted into carbolic acid (hydrated oxide of phenyle) and ammonia, which are, however, accompanied by traces of aniline. Salicylamide, $\text{C}_{14}\text{H}_5\text{O}_4 + \text{NH}_2$, contains the elements of anthranilic acid, and when it yields carbolic acid and ammonia, a part of it is decomposed, in order to furnish the elements of water to the rest, so that a residue of carbon is left.



The formation of carbolic acid in this process, and the fact that aniline is also formed, indicate a relation between these compounds, such as has been already noticed.

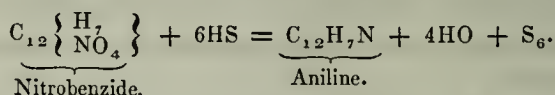
3. Aniline is formed when nitrobenzide is distilled with an alcoholic solution of potash. It is accompanied in this case by the remarkable compound azobenzide and by oxalic acid. Hofmann has shewn that the action here is between the elements of nitrobenzide and those of alcohol. The following equation shews how this may take place:—



but other substances are formed, and therefore the whole action is in reality more complex.

4. Aniline is formed, as has already been stated, by the action of

sulphuretted hydrogen and ammonia on an alcoholic solution of nitrobenzide. The reaction is explained in the following equation:—



Such are the different modes in which aniline is formed, and they are interesting, as shewing how alkaloids may be obtained.

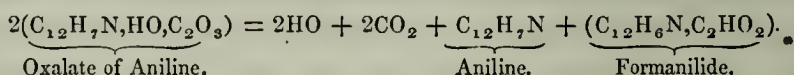
Aniline, as a base, is entirely analogous to ammonia. Thus, it unites directly with the hydrogen acids; but, when it combines with oxygen acids, 1 eq. of water is taken up. It also forms double salts with bichloride of mercury, bichloride of platinum, and other similar compounds, as ammonia does.

The remarkable analogy between aniline and ammonia is further seen in the existence and mode of formation of certain compounds derived from aniline, and analogous to urea, oxamide, and carbamide.

Oxanilide is formed by the action of heat on oxalate of aniline. The oxalate, $\text{C}_{12}\text{H}_7\text{N}, \text{HO} + \text{C}_2\text{O}_3$, loses 2 eq. of water, and yields oxanilide, $\text{C}_{12}\text{H}_6\text{N} + \text{C}_2\text{O}_2$, analogous to oxamide, $\text{NH}_2 + \text{C}_2\text{O}_2$. It is insoluble in ether and water, and very sparingly soluble in absolute alcohol. Formula, $\text{C}_{14}\text{H}_6\text{NO}_2$. It is acted on by acids and alkalies in a manner exactly analogous to what is observed in oxamide.

Formanilide.—This compound is formed in the same process as the last, along with aniline and carbonic acid. It is soluble in cold alcohol, and may thus be separated from the oxanilide. The analogous compound of ammonia, *formamide*, is not known; but its formula would be $\text{NH}_2 + \text{C}_2\text{HO}_2$. That of formanilide is $\text{C}_{12}\text{H}_6\text{N} + \text{C}_2\text{HO}_2 = \text{C}_{14}\text{H}_7\text{NO}_2$. It is decomposed by acids, yielding salts of aniline and free formic acid; and by alkalies, yielding formiates and free aniline.

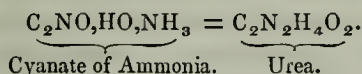
As the formation of oxanilide is accompanied by that of formanilide, aniline, carbonic acid, and water, the probable explanation is, that while 1 eq. of oxalate of aniline yields 1 eq. oxanilide and 2 eq. water, 2 eq. of oxalate of aniline are resolved at the same time into 1 eq. formanilide, 1 eq. aniline, 2 eq. carbonic acid, and 2 eq. water. The following equation expresses this last change:—



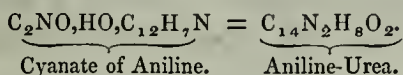
These remarkable compounds were discovered by Gerhardt.

Aniline-urea.—Hofmann has shewn that when cyanic acid is made to combine with aniline, the salt first formed soon undergoes, like the cyanate of ammonia, a spontaneous change, by which it is converted into a crystalline compound analogous to urea, and no longer containing

aniline or cyanic acid, while its composition is the same as that of hydrated cyanate of aniline. In the case of urea we have



In the case of aniline we have



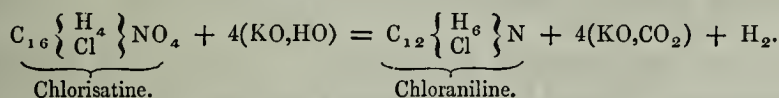
Carbanilide.—Hofmann has also described a compound, $C_{13}H_6NO$, which is aniline in which 1 eq. of hydrogen is replaced by 1 eq. of carbonic oxide, $C_{12}\left\{\begin{smallmatrix} H_6 \\ CO \end{smallmatrix}\right\}$. It is analogous to carbamide, $N\left\{\begin{smallmatrix} H_2 \\ CO \end{smallmatrix}\right\} = CO, NH_2$, a body only known as yet in combination, and may be called, therefore, *carbanilide*. It is formed by the action of chlorocarbonic acid (phosgene) gas on aniline, and yields very fine prismatic crystals.

Hofmann has described another new compound, not yet named, formed by the action of bisulphuret of carbon on aniline. Its formula is $C_{13}H_6NS$, that is, aniline in which 1 eq. of hydrogen is replaced by 1 eq. of a sulphuret of carbon corresponding to carbonic oxide, $C_{12}\left\{\begin{smallmatrix} H_6 \\ CS \end{smallmatrix}\right\}$; or carbanilide in which the oxygen is replaced by sulphur.

It has also been shewn by Hofmann that the action of aniline on the chlorides of phosphorus and of silicon, and on oil of mustard, is closely analogous to that of ammonia.

We have now to consider, briefly, a series of alkaloids derived from aniline, in which the hydrogen is replaced by chlorine, bromine, or nitrous acid.

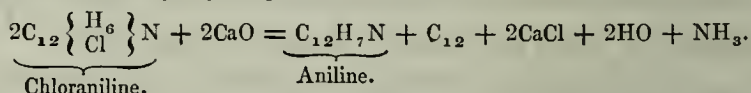
Chloraniline.—Discovered by Hofmann. It is obtained by distilling chlorisatine with potash, in the same way as aniline is formed from isatine. The reaction is very simple:—



Chloraniline forms colourless regular octohedral crystals, modified like those of alum, which melt at 148° , and solidify at 134° . It is very volatile, and evaporates at all temperatures. Its tendency to crystallize is very strong. In taste and smell it cannot be distinguished from aniline. It is heavier than water, and boils at a temperature approaching 400° , being at the same time partially decomposed. It is very sparingly soluble in water, soluble in alcohol and ether. Its solutions act feebly on dahlia paper, but its basic character is quite distinct. It unites with acids, forming salts which crystallize with the greatest fa-

cility. For details in regard to these, the reader is referred to Dr. Hofmann's paper, *Ann. der Ch. und Ph.*, liii. 1. Like ammonia, aniline, and other organic bases, chloraniline unites directly with hydrogen acids, and takes up 1 eq. of water in combining with oxygen acids. Like all organic bases it forms a double chloride with bichloride of platinum. It agrees with aniline, likewise, in striking a deep yellow colour when its solution in hydrochloric acid is placed in contact with fir wood.

In short, chloraniline is as truly an organic base or alkaloid as aniline, or any other alkaloid whatever, and it is specially interesting as being the first example of a base containing chlorine in replacement of hydrogen. Its mode of formation, as well as the perfect analogy which it presents to aniline, demonstrate that it is formed from that base by substitution, and that the chlorine, occupying here the position of hydrogen, loses much of its negative energy, while the type of the compound remains unaltered. That the type is not changed appears by the basic properties, and also by the fact that chloraniline when passed over red-hot lime is reconverted into aniline, one part being decomposed to yield the necessary hydrogen to the other.



Dichloraniline.—When bichlorisatine (dichlorisatine) is distilled with potash another base is formed, which has not been fully investigated. From the analogy of the bromine compound it is believed to be dichloraniline, $C_{12}\left\{\begin{smallmatrix} H^5 \\ Cl_2 \end{smallmatrix}\right\}N$. It crystallizes in prisms, and is probably a feebler base than chloraniline.

When aniline, chloraniline, or dichloraniline is acted on by chlorine, there is formed *trichloraniline*, $C_{12}\left\{\begin{smallmatrix} H^4 \\ Cl_3 \end{smallmatrix}\right\}N$, a body already mentioned, and formerly called *chlorindatmit*. It has no basic properties, the amount of chlorine being apparently too large for this. It is accompanied by chlorophenismic and chlorophenusic acids.

The action of bromine on chloraniline gives rise to the formation of a crystalline compound, *chlorodibromaniline* $= C_{12}\left\{\begin{smallmatrix} H^4 \\ Cl \\ Br_2 \end{smallmatrix}\right\}N$, which, like trichloraniline, is neutral.

It is probable, according to Hofmann, that chloraniline, when acted on by nitric acid, yields an acid analogous to nitropicric acid, but containing 1 eq. of chlorine, in replacement of 1 eq. of hydrogen. The

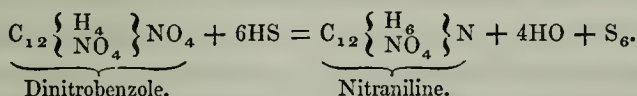
formula of this acid is $C_{12} \left\{ \begin{array}{c} H \\ Cl \\ 3NO_4 \end{array} \right\} O, HO$; and its proper name would be *nitrochloropicric acid*, or *nitrochlorophenosic acid*.

Bromaniline.—When bromisatine is distilled with potash it yields this base, which is in every respect analogous to chloraniline, crystallizing with great facility in octohedrons. Its formation is explained as that of chloraniline. Formula, $C_{12} \left\{ \begin{array}{c} H_6 \\ Br \end{array} \right\} N$.

Dibromaniline.—This compound is formed when bibromisatine is distilled with potash. It is a base, crystallizing in flat, four-sided rhombic prisms, soluble in alcohol. Its formula is $C_{12} \left\{ \begin{array}{c} H_5 \\ Br_2 \end{array} \right\} N$.

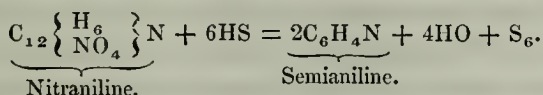
The direct action of bromine on aniline gives rise to the formation of *tribromaniline*, $C_{12} \left\{ \begin{array}{c} H_4 \\ Br_3 \end{array} \right\} N$, which is no longer basic. It is the substance formerly called *bromaniloid*. It is possible, as Hofmann remarks, that, if tribromisatine and trichlorisatine were known, these compounds might yield by distillation with potash a compound isomeric with tribromaniline, and possessing basic characters.

Nitraniline.—This compound, discovered by Hofmann and Muspratt, has not yet been obtained from aniline or from isatine. But it is formed when an alcoholic solution of binitrobenzide (dinitrobenzole) is acted on by ammonia and sulphuretted hydrogen. Its formation is quite analogous to that of aniline from nitrobenzole (nitrobenzide).



Nitraniline forms fine golden yellow prisms, soluble in hot water, in alcohol, and in ether. It is fusible and volatile, and has an aromatic smell when heated, and a burning sweet taste. It is a weak base, but agrees with aniline, chloraniline, &c. in colouring fir wood yellow with the aid of an acid. Its salts are crystallizable, and have the same constitution as those of ammonia and of aniline.

According to Zinin, the action of sulphuretted hydrogen on dinitrobenzole, when carried further, gives rise to the formation of another base, *semianiline* = C_6H_4N . This is probably formed from nitraniline as follows:—



But this compound has not been fully investigated.

By the action of bromine on nitraniline there is formed a neutral compound, *nitrodibromaniline*, analogous to trichloraniline, tribromaniline, and chlorodibromaniline. Its formula is $C_{12} \left\{ \begin{array}{c} H_4 \\ Br_2 \\ NO_4 \end{array} \right\} N$.

The following table will shew the relation between aniline and the derivatives of it described in the preceding pages:—

Aniline.	C_{12}	$\left\{ \begin{array}{c} H_7 \\ \end{array} \right\}$	N	basic.	Amaphenase.
Chloraniline	C_{12}	$\left\{ \begin{array}{c} H_6 \\ Cl \end{array} \right\}$	N	basic.	Amachlophenese.
Dichloraniline	C_{12}	$\left\{ \begin{array}{c} H_5 \\ Cl_2 \end{array} \right\}$	N	basic.	Amachlophenise.
Trichloraniline	C_{12}	$\left\{ \begin{array}{c} H_4 \\ Cl_3 \end{array} \right\}$	N	neutral.	Amachlophenose.
Bromaniline	C_{12}	$\left\{ \begin{array}{c} H_6 \\ Br \end{array} \right\}$	N	basic.	Amabrophenese.
Dibromaniline	C_{12}	$\left\{ \begin{array}{c} H_5 \\ Br_2 \end{array} \right\}$	N	basic.	Amabrophenise.
Tribromaniline	C_{12}	$\left\{ \begin{array}{c} H_4 \\ Br_3 \end{array} \right\}$	N	neutral.	Amabrophenose.
Chlorodibromaniline	C_{12}	$\left\{ \begin{array}{c} H_4 \\ Cl \\ Br_2 \end{array} \right\}$	N	neutral.	Amachlobrophenose.
Nitraniline	C_{12}	$\left\{ \begin{array}{c} H_6 \\ NO_4 \end{array} \right\}$	N	basic.	Amanitrophenese.
Nitrodibromaniline	C_{12}	$\left\{ \begin{array}{c} H_4 \\ Br_2 \\ NO_4 \end{array} \right\}$	N	neutral.	Amanitrobrophenose.

It is evident from this table that the hydrogen of aniline may be partially replaced by chlorine, bromine, and even by nitrous acid, while the basic character of the type continues to exist.

Picoline.—This base was lately discovered in coal tar by Dr. T. Anderson. It occurs along with aniline and leucoline, from which, being more volatile, it is separated by rectification. It is a colourless, mobile, oily fluid, of sp. gr. 0.955 at 50°, boiling at 272°. It dissolves in water, but is separated by the addition of potash.

It is a powerful base, quite distinct from aniline, as it neither strikes a blue with bleaching liquor, nor a yellow with fir wood. It has a powerful, penetrating, and disagreeable smell; and it is owing to the presence of picoline that impure aniline from coal tar has an unpleasant odour, which disappears when it is purified. It would appear that the base called *odorine*, found in animal empyreumatic oil by Unverdorben, consisted chiefly of picoline.

With acids picoline forms salts which are crystallizable, but not with the same facility as those of aniline. It has a tendency to form acid salts.

Anderson has obtained, by his analysis of picoline, the remarkable result that it is isomeric with aniline, and strictly so, its atomic weight being the same. Its formula is, of course, $C_{12}H_7N$. For the proba-

ble relation between aniline and picoline, see the sections on Chlonaph-tase and Chlonaphtese, pp. 1247 et seq.

Leucoline. Syn. Quinoline.—This base was first observed in coal tar by Runge, and afterwards obtained as a product of the distillation of quinine, cinchonine, and strychnine with potash by Gerhardt. Hofmann shewed that the two compounds were identical. Leucoline or quinoline is found in the less volatile portions of the basic oil of coal tar. It is purified by rectification, picoline and aniline being carried off in the first portions which pass over. Its boiling point is 460° , and its sp. gr. is 1.081. It is oily, colourless, has a very high dispersive and refractive power, equal to that of bisulphuret of carbon, a rather unpleasant smell, and a burning taste.

When prepared by Gerhardt's process it is not accompanied by picoline and aniline. With acids it forms salts, which crystallize, but with much greater difficulty than those of aniline. These salts, however, correspond in constitution to those of ammonia, aniline, or organic bases in general. The formula of leucoline is $C_{18}H_8N$.

Such are the alkaloids hitherto described as occurring in coal tar. Runge observed another, which he called *pyrrole*, and which Anderson also met with, but in too small a quantity for investigation. Its composition is unknown. Anderson has recently detected another base in animal empyreumatic oil, in which, moreover, Unverdorben long ago described, besides crystalline (aniline) and odorine (picoline?), two other bases, *animine* and *olanine*. But these are also comparatively unknown.

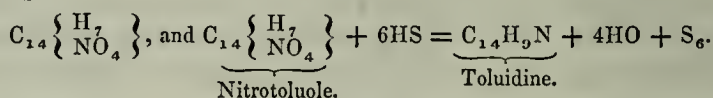
The most remarkable point about the bases of coal tar, two of which, aniline and leucoline, have also been obtained in other ways, is this, that in composition they approach very closely to the volatile vegetable bases, nicotine and conicine; while in properties they are also very analogous to these compounds. The following table shews the composition of the oily bases, natural and artificial:—

Nicotine	.	.	$C_{10}H_8N$	} Natural oily bases.
Conicine	.	.	$C_{16}H_{16}N$	
Aniline	.	.	$C_{12}H_7N$	
Picoline	.	.	$C_{12}H_7N$	} Artificial oily bases.
Leucoline	.	.	$C_{16}H_8N$	

It will be seen that they are all alike devoid of oxygen; and it is remarkable that the artificial oily bases seem, like the natural ones, to be poisonous. Since aniline has been obtained by various transformations from compounds of the benzole ($C_{12}H_6$) series, and the phenyle ($C_{12}H_5$) series, if, indeed, these two series be not essentially one, characterized by 12 eq. of carbon, it can hardly be doubted, that, when we shall have become acquainted with compounds of the series with 10 or that with 16 eq. of carbon, we shall be able, by some of the processes which

yield aniline, or by new methods, to produce artificially nicotine and conicine.

Toluidine.—This base, discovered by Hofmann and Muspratt, is obtained by the action of ammonia and sulphuretted hydrogen on an alcoholic solution of nitrotoluole (nitrotoluide, protonitrobenzoëne), as aniline is from nitrobenzole, and nitraniline from dinitrobenzole. The fundamental compound of the series is toluole = $C_{14}H_8$. Nitrotoluole is



Toluidine is in taste and smell exactly similar to aniline. It is solid, but very fusible, melting at 104° to a highly refracting iridescent oil, boiling at 388° , and when cooled consolidating into a crystalline mass. Toluidine has an alkaline reaction on reddened litmus and on dahlia paper. It evidently belongs to the same class of bases as aniline; for, besides its oily character when fused, its smell and taste, and its high refractive power, it also, like aniline, turns fir wood yellow with the aid of an acid. Both in regard to composition and properties, it may be added to the table of artificial oily bases just given.

Its salts are distinguished by the same tendency to crystallize with facility as those of aniline.

With bromine toluidine yields a crystalline compound, apparently tribromotoluidine, $C_{14} \left\{ \begin{smallmatrix} H_6 \\ Br_3 \end{smallmatrix} \right\} N$. Chlorine seems to form an analogous compound.

The formation of toluidine from the carbo-hydrogen toluole supplies an additional argument in favour of the probability of our discovering hereafter the means of producing nicotine and conicine artificially, provided we can obtain the corresponding carbo-hydrogens, $C_{10}H_6$ and $C_{16}H_{15}$.

Furfurine.—This base was obtained by Fownes from furfurole, an oily liquid formed by the action of sulphuric acid on bran. This oil, $C_{15}H_6O_6$, when acted on by ammonia, yields a crystalline compound, *furfurolamide*, analogous to hydrobenzamide, the formula of which is $C_{15}NH_6O_3$. When this compound is dissolved in hot potash, it is converted into a basic compound of the same composition, just as hydrobenzamide is into amarine. In the furfurine the atomic weight is double that of the furfurolamide; or, at all events, the formula of the base is $C_{30}N_2H_{12}O_6$. It is soluble in hot water, and crystallizes on cooling, very soluble in alcohol and ether, and it acts strongly on vege-

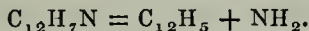
table colours. When boiled with salts of ammonia, it expels that alkali, and it forms with acids crystallizable salts, several of which have been analyzed by Fownes. They have the usual constitution of the salts of alkaloids. In composition furfurine approaches very closely to several of the vegetable bases.

Cotarnine, $C_{25}NH_{13}O_6$, and *Narcogenine*, have been already described under Narcotinc, from which they are derived. *Amarine*, *Picrine*, and *Lophine* have been also described among the derivatives of oil of bitter almonds.

We have now gone through the artificial as well as the natural alkaloids, and the present is the proper place to say a few words concerning the constitution of this class of compounds. Of the constitution of the vegetable bases nothing certain is known; but the modes of formation of the artificial alkaloids have suggested certain views as possible, or even probable.

In the first place, it may be considered very probable that all alkaloids are formed by substitution from other substances, as, for example, aniline from nitrobenzole, and toluidine from nitrotoluole.

In the next place, some of the alkaloids may be viewed as compounds of amide, as, for example, aniline, which has the composition of phenylamide,



The other artificial bases analogous to aniline may be regarded in the same way; leucoline as $C_{18}H_6 + NH_2$, or toluidine as $C_{14}H_7 + NH_2$; being derived, on this view, by substitution of amide either for hydrogen in the carbo-hydrogens $C_{12}H_6$, $C_{18}H_7$, and $C_{14}H_8$, or for nitrous acid in the compounds $C_{12}\left\{\begin{smallmatrix} H_5 \\ NO_4 \end{smallmatrix}\right\}$, $C_{18}\left\{\begin{smallmatrix} H_6 \\ NO_4 \end{smallmatrix}\right\}$, and $C_{14}\left\{\begin{smallmatrix} H_7 \\ NO_4 \end{smallmatrix}\right\}$. This class of alkaloids, which contain no oxygen, seem to have the simplest constitution.

But, thirdly, there is among the artificial alkaloids a substance which may be taken as the type of a somewhat more complex class, in which the hydrogen of the fundamental compound of the series has been replaced by some compound of nitrogen and oxygen. This substance is nitraniline, which is $C_{12}N_2H_6O_4 = C_{12}\left\{\begin{smallmatrix} H_6 \\ NO_4 \end{smallmatrix}\right\}N$.

Fresenius suggests that many of the natural alkaloids, containing 4 eq. of oxygen and 2 of nitrogen, may have a constitution analogous to that of nitraniline, in which 1 eq. of hydrogen is replaced by 1 eq. of nitrous acid. For example, strychnine, $C_{44}N_2H_{23}O_4$, may be

$C_{44}\left\{\begin{smallmatrix} H_{23} \\ NO_4 \end{smallmatrix}\right\}N$. Quinine, menispermine, staphisaine, and delphine, may all be associated with strychnine.

Chelidonine, $C_{40}N_3H_{20}O_6$, may be, according to Fresenius, binitrichelidonine, $C_{40}\left\{\begin{smallmatrix} H_{20} \\ 2NO_3 \end{smallmatrix}\right\}N$.; 2 eq. of hydrogen being replaced by 2 eq. of hyponitrous acid.

Where the alkaloid contains 2 eq. of oxygen and 2 of nitrogen, the replacing body may be deutoxide of nitrogen. Thus, caffeine, $C_8N_2H_5O_2$, may be nitre-caffeine, $C_8\left\{\begin{smallmatrix} H_5 \\ NO_2 \end{smallmatrix}\right\}N$; and to this class would belong cinchonine and sinapoline. Urea may be added, as it may be $C_2\left\{\begin{smallmatrix} H_4 \\ NO_2 \end{smallmatrix}\right\}N$.

Another class may contain protoxide of nitrogen as replacing substance. Thus, harmaline, $C_{24}H_{13}N_2O$, may be nitra-harmaline, $C_{24}\left\{\begin{smallmatrix} H_{13} \\ NO \end{smallmatrix}\right\}N$; and theobromine, $C_9H_5N_3O_2$, may be binitra-theobromine, $C_9\left\{\begin{smallmatrix} H_5 \\ 2NO \end{smallmatrix}\right\}N$.

Lastly, hydrogen may even be supposed to be replaced by nitric acid; and, on this supposition, jervine, $C_{60}H_{45}N_2O_5$, might be nitrujervine, $C_{60}\left\{\begin{smallmatrix} H_{45} \\ NO_5 \end{smallmatrix}\right\}N$.

The bases above mentioned, if such be their true constitution, are derived from radicals containing no oxygen, as aniline from benzole, &c. But there are others, which are probably derived from radicals containing oxygen. Such bases are morphine, codeine, narcotine, and others. Of these, however, in this point of view so little is known, that, as Fresenius observes, it is safest, for the present, to consider them as simple alkaloids, analogous to aniline, nicotine, or sinnamine.

The views of Fresenius have a high degree of probability, and will probably aid in enabling us to discover the true nature of the alkaloids. He points out that, on his theory, various facts connected with the alkaloids are easily explained. Thus, for example, it is easy to see on his theory, that when heated with potash ammonia is not given off; that their power of saturation cannot be proportional to their amount of oxygen or of nitrogen, as it is well known not to be. On the other hand, it appears to be proportional to the amount of nitrogen which is not in the form of an oxygen compound, such as NO , NO_2 , NO_3 , NO_4 , or NO_5 . This nitrogen generally, perhaps always, amounts to 1 eq. in 1 eq. of the base, as may be seen in Fresenius' formulæ. The simple

alkaloids, such as aniline, contain only that 1 eq. of nitrogen, just as ammonia does.

It must here be remarked that the alkaloids all appear to be of the same general type with ammonia, and that, like ammonia, they unite directly with hydrogen acids, while, to combine with oxygen acids, they take up 1 eq. of water. This leads to the conclusion, that if, in the case of ammonia, there is formed a compound analogous to metals, ammonium, which unites with salt radicals, while its oxide combines with oxygen acids, the same is probably true of the alkaloids. Thus, when ammonia acts on hydrochloric acid, we have $\text{NH}_3 + \text{HCl} = \text{NH}_4 + \text{Cl}$, chloride of ammonium, and when aniline combines with the same acid, we may suppose the change to be analogous; $\text{C}_{12}\text{H}_7\text{N} + \text{HCl} = \text{C}_{12}\text{H}_8\text{N} + \text{Cl}$, chloride of anilium. Again, sulphate of ammonia, $\text{NH}_3, \text{HO}, \text{SO}_3$, is usually considered to be sulphate of oxide of ammonium, $\text{NH}_4, \text{O} + \text{SO}_3$; and so, in like manner, sulphate of aniline, $\text{C}_{12}\text{H}_7\text{N}, \text{HO}, \text{SO}_3$, is probably sulphate of oxide of anilium, $\text{C}_{12}\text{H}_8\text{N}, \text{O} + \text{SO}_3$. If true of one, this is probably true of all.

Such is the present state of our knowledge with regard to the alkaloids; and, although it is still very imperfect, yet it is evident that we are now making some progress in this department of science, and may hope speedily to advance much farther.

NEUTRAL OR INDIFFERENT COMPOUNDS WHICH OCCUR GENERALLY IN VEGETABLES.

Under this head we have to consider certain substances, namely, starch, gum, and woody fibre, which are found in every plant, and constitute the principal mass of the vegetable kingdom.

Starch. Syn. Fecula; Amylon.—Formula of starch dried at the ordinary temperature, $\text{C}_{12}\text{H}_9\text{O}_9, \text{HO} + 2\text{aq}$. Dried at 212° , $\text{C}_{12}\text{H}_9\text{O}_9, \text{HO}$. Formula of its compound with oxide of lead, $\text{C}_{12}\text{H}_9\text{O}_9, 2\text{PbO}$. (Payen.)

Starch occurs abundantly in the seeds of the cerealia; in many roots, such as the potato, and arrow-root, the root of *Marantha arundinacea*; in the stems of many monocotyledonous plants, such as palms; and in several lichens. It is also found, according to Liebig, in unripe apples and pears, and in the seeds of leguminous plants. It is most easily obtained pure from potatoes.

Starch forms small round brilliant grains, varying in size from $\frac{1}{200}$ th to $\frac{1}{10000}$ th of an inch in diameter. These are composed of concentric layers or membranes, of which the outer one is the thickest. When starch is dried at 140° , it forms translucent grains of a larger size formed by the rapid drying of the jelly which it forms with water.

This is the case with sago and tapioca, which are nearly pure starch: the former from the pith of a palm, *Sagrus Rumphii*; the latter from the juice of *Iatropa manihot*, which, although poisonous, deposits on standing a powder which is inert, being starch.

The starch of wheat-flour is contaminated with gluten, which is removed by fermentation, an acid being produced; or, still better, by the action of a weak alkaline solution.

Starch, when pressed in the fingers, gives out a peculiar sound. It is insoluble in cold water, but dissolved by hot water into a stiff jelly, which is much used for stiffening linen. It is dissolved by diluted acids; and, when this solution is boiled, it undergoes a remarkable series of changes. Thus, pure starch is coloured blue by iodine. When its solution in diluted acids has been boiled for some time it is coloured purple by iodine; and, after a still longer interval, iodine ceases to colour it. In the latter case the starch is found to be converted into a substance soluble in cold water, and having most of the properties of gum. This is called *Dextrine*, and has exactly the composition of starch.

By a boiling still longer continued the dextrine is destroyed, and converted into starch-sugar, or grape-sugar.

When heated with moderately strong nitric acid, starch is converted into oxalic acid, and other acids not exactly ascertained, but yields no mucic acid. Starch forms a soluble compound with potash, and insoluble compounds with oxide of lead, lime, and baryta.

When starch is bruised, by grinding it with some hard powder, the outer envelope of the grains is broken, and if now placed in water it swells up into a jelly. The same change takes place when starch is thrown into water at 140° . The envelopes burst, and a jelly is formed. But the starch is not dissolved; for, if the jelly be placed on bibulous paper, it shrinks up from the loss of water, and leaves a horny mass, insoluble in cold water, but easily soluble with the aid of heat. The outer coating is generally left undissolved, and amounts to 0.003 or 0.004 of the starch, but may be dissolved by long boiling. The gelatinous starch has been called *Amidine*, but its composition is the same as that of starch.

According to the recent experiments of Jaquelain, (*Ann. de Ch. et de Phys.* lxiii. 167,) when starch is heated in a digester with 5 to 15 parts of water, to 302° , everything is dissolved but the outer coats; and the solution, which is quite thin, deposits, on cooling, starch in minute granules, $\frac{1}{12700}$ th of an inch in diameter. These are more soluble than the original starch, and are coloured blue by iodine. Their composition is the same as that of starch dried at 212° ; but Jaquelain states that starch in all forms contains about 0.25 per cent. of nitrogen,

which he considers essential. The formation of these granules indicates the presence of some organic property, and in common starch the structure shews this still more distinctly. This degree of organization is one of the most important characters of starch.

With bromine starch forms an orange compound; with iodine, as already mentioned, a blue one. This latter, when pure, is not crystallized; and, although some consider it a definite compound, it is more probable that its colour is owing to finely-divided iodine mechanically mixed with starch, or combined with it in the same way as a dye-stuff is united to the fibre of cloth.

Dextrine.—This substance is formed either by the action of diluted acids on starch at the boiling temperature continued for a certain time, or by the action of an infusion of malt on a solution of starch kept for some time at 150°. The addition of alcohol precipitates the dextrine. There appear to be two varieties; one coloured reddish purple by iodine, the other not coloured by that reagent.

Its name is derived from the action of its solution on polarized light, as it causes the plane of polarization to deviate to the right. (Biot.) Its solution is not gelatinous, and it resembles gum. Its composition is the same as that of starch.

By the action of hot diluted acids, or of an infusion of malt, dextrine is finally converted into grape-sugar.

When dry starch is roasted, it is converted into a brownish transparent gum, soluble in cold water, and much used in calico-printing. This is probably identical with dextrine.

Diastase.—This name has been given to the substance contained in malt which effects the conversion of starch into dextrine and grape-sugar. It is precipitated from a cold infusion of malt by the addition of alcohol, as a white powder, soluble in water and tasteless. It contains nitrogen, and is probably analogous to gluten; but its composition, in a state of purity, is not known. It is said that 1 part of diastase will convert into sugar 2000 parts of starch. Its action probably depends on its undergoing spontaneous decomposition or putrefaction in contact with the starch, just as the conversion of sugar into alcohol and carbonic acid is caused by the putrefaction of gluten, &c. It is remarkable that its first effect seems to be to separate the external coat from the grains of starch.

The amount of diastase in malted barley is but small, not more than $\frac{1}{500}$ th part. It is, however, by the action of this small proportion that the starch of the barley is converted into sugar in the first stage of brewing, preparatory to the fermentation by which ale or malt spirits is obtained.

Inuline.—This variety of starch occurs in the root of *Inula Helenium*, in some lichens, and in the root of the dahlia. It is very soluble in hot water; but, if moderately diluted, does not, like common starch, gelatinize on cooling. Its solution is not coloured blue by iodine; but, if so far concentrated as to deposit some of the starch on cooling, the addition of tincture of iodine to the hot solution yields a blue colour after cooling. (Liebig.)

The formula of inuline is $C_{24}H_{21}O_{21}$; and with oxide of lead it forms two compounds, $C_{24}H_{21}O_{21}, 5PbO$, and $C_{24}H_{18}O_{18}, 3PbO$. (Parnell.) As the formula of inuline in the latter compound is exactly twice that of starch, these results require confirmation.

Moss or Lichen Starch.—This is found in *Cetraria islandica* and other lichens. It forms a white opaque jelly. Its solution, if moderately diluted, is not coloured blue by iodine; but if it be concentrated so as to gelatinize on cooling, and tincture of iodine added to the hot liquid, the jelly is coloured blue. (Liebig.) This reaction is favourable to that view which considers the blue produced by iodine as not a compound, but starch dyed by iodine.

According to Guerin-Varry, the formula of this variety of starch is $C_{10}H_{11}O_{10}$.

Starch is one of the most important substances in the vegetable kingdom. Its ready convertibility, without change of composition, into soluble forms, such as dextrine and sugar, adapt it admirably for carrying on those changes which occur in the juices of vegetables. It is stored up in the seeds, roots, and pith of plants, and by its decomposition furnishes the materials for many of the most essential vegetable products. It also serves as a most important element of the food of animals, furnishing not indeed the means of increase of mass, but the materials for keeping up respiration, and supplying the animal heat. The fats and fixed oils of the vegetable as well as the animal kingdom are in all probability derived principally from the deoxidation of starch.

Gum occurs in almost all vegetable juices, and frequently exudes in drops from the bark of trees, especially *Acacia* and *Prunus*. Formula $C_{12}H_{11}O_{11}$.

Gum forms irregular, amorphous, transparent masses, sometimes nearly colourless, often yellow and brown. It is soluble in cold water, forming a mucilaginous solution, from which alcohol precipitates the gum. Subacetate of lead also causes a white precipitate. By the action

of a heat of 266° gum loses 1 at. of water, but is changed in its properties. Strong nitric acid converts it into mucic acid.

Gum Tragacanth differs from ordinary gum in being insoluble in cold water, with which it swells up into a mucilaginous mass. With boiling water it forms a mucilage like that of ordinary gum.

Gum is much used in preparing water-colours, in calico-printing, and in medicine as a demulcent.

Woody Fibre, or Lignine.—This name is given to the fibrous matter which forms the basis of wood, and of the stems and leaves of herbaceous plants. It is insoluble in all ordinary solvents, and is left after vegetables have been exposed to the successive action of ether, alcohol, water, diluted acids, and diluted alkalis.

According to Prout, the formula of lignine, when dried between 300° and 350° , is $C_{12}H_8O_8$. It forms about 95 per cent. of baked wood, and is the chief ingredient of linen, paper, and cotton. According to Payen, the tissue of wood is composed of $C_{12}H_{10}O_{10}$, and is isomeric with starch; while pure lignine fills the cells, and is $C_{35}H_{24}O_{20}$.

The composition of wood differs but little from that of lignine. Oak wood, according to Gay-Lussac and Thenard, is $C_{36}H_{22}O_{22}$. But wood contains mineral substances, which form its ashes when it is burned.

When lignine, in the form of straw, &c., is mixed with oil of vitriol, there is produced, besides dextrine or a substance resembling it, an acid, lignosulphuric acid, which forms soluble salts with baryta and oxide of lead. The dextrine, by boiling with the acid, is converted into grape-sugar. In strong nitric acid saw-dust dissolves; and, on the addition of water, a white insoluble powder is deposited, which contains nitric acid, and explodes when heated. (Robiquet.)

Gun-Cotton. Xyloidine.—When woody fibre, in the form of cotton, paper, tow, sawdust, &c., is immersed for about two minutes in fuming nitric acid, or into a mixture of nitric acid and oil of vitriol, and then squeezed out and well washed, it appears little altered; but when dried by a gentle heat it is found to be converted into a highly-explosive compound, containing the elements of lignine and of nitric acid.

Schönbein first proposed to employ the compound formed from cotton as a substitute for gunpowder, and called it gun-cotton, or explosive cotton. It was, however, previously known that paper, and other forms of lignine, and even starch, when dissolved in nitric acid, yielded on the addition of water a precipitate, to which the name of *Xyloidine* was given, and which, when heated to 356° , deflagrated with violence. (Braconnot, Pelouze.)

It would appear that, although both compounds are explosive, they are quite different in composition, for xyloidine may be considered as starch, $C_{12}H_{10}O_{10}$, in which 2 eq. of hydrogen are replaced by 2 eq. of nitrous acid, and its formula is, therefore, $C_{12}\left\{\begin{smallmatrix} H_8 \\ 2NO_4 \end{smallmatrix}\right\}O_{10}$; while gun-cotton appears to be composed of 1 eq. of lignine and 4 eq. of nitric acid, or of 1 eq. of an oxide of lignine and 4 eq. of hyponitrous acid. Its formula in the former case will be $C_{12}H_8O_8 + 4NO_5$; in the latter, $C_{12}H_8O_{16} + 4NO_3$. (Porrett and Teschemacher.)

It is obvious that if the xyloidine from starch and that from lignine be the same substance, the formula of that compound, as derived from that of lignine, $C_{12}H_8O_8$, would be $C_{12}H_8O_8 + 2NO_5$, or $C_{12}H_8O_{10} + 2NO_4$, or, finally, $C_{12}H_8O_{12} + 2NO_3$; and thus, while the analogy between xyloidine and gun-cotton is obvious, the superior explosive power of the latter is shewn to depend on the greater proportion of nitric, nitrous, or hyponitrous acid, in short, of oxygen, which it contains.

Gun-cotton is easily prepared on the small scale by immersing for two minutes 1 part of clean dry cotton wool in about 10 parts, or as much as suffices to cover and moisten it completely, of a mixture of equal volumes of oil of vitriol, sp. gr. 1·840, and nitric acid, sp. gr. 1·510. The cotton is then gently pressed, to expel the greater part of the adhering acid, and washed with cold water till the water comes off tasteless. It is then dried by a very gentle water heat; and when dry it is not perceptibly altered in appearance. But it is found to have increased considerably in weight, 100 parts of dried cotton yielding about 169·5 of dry gun-cotton, of which 102·5 are nitric acid or its elements, taken up by the cotton, and the remainder, 67 parts, represents the cotton, minus $\frac{1}{3}$ of its original weight, which has been given off as water, while the anhydrous cotton, or lignine, combined with the acid.

Porrett is of opinion that in gun-cotton the acid is neutralized by an oxide of lignine, which he supposes to be a powerful base; but, although the gun-cotton is neutral to test-paper, this may depend on its insolubility, and there is not sufficient evidence of the existence of the supposed base.

When heated to a point not very far above the boiling-point of water, and far below that at which gunpowder explodes, or when touched with a spark, gun-cotton explodes instantaneously, and, when of good quality, leaves hardly any visible residue.

It is probable that gun-cotton possesses a greater explosive force than an equal weight of gunpowder; but its preparation is not only much more expensive, but difficult and uncertain, owing to the variable quality of the cotton, and, in particular, to the difficulty of moistening

every part of it equally with the strong acid, without causing some parts to be too long in contact with the acid. Even on the small scale it is not easy to prepare gun-cotton of uniform quality. Good gun-cotton, however, from its exploding more rapidly than gunpowder, will probably be found useful in the blasting of rocks, although it should not turn out to be preferable for fire-arms.

Mould ; Humus.—When exposed to air and moisture, wood suffers decay or *eremacausis*, and is said to moulder, being gradually converted into a dark brown or black powder, called Mould, or sometimes Humus. The longer the decay has operated, the greater is the proportion of carbon in the residue. Thus oak wood is $C_{36}H_{22}O_{22}$; and one specimen of oak humus, analyzed by Meyer, was found to contain $C_{35}H_{20}O_{20}$; and another, examined by Will, $C_{34}H_{18}O_{18}$: shewing that, for every two equivalents of hydrogen oxidized by the air, one equivalent of carbonic acid had separated.

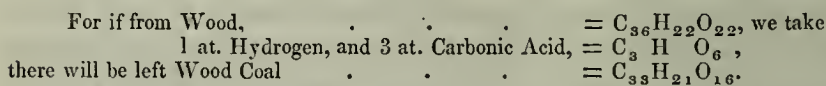
This decay of wood is prevented by antiseptics, and especially by corrosive sublimate, which seems to combine with the lignine. Were the decay to continue till all the hydrogen had been removed, wood, $C_{36}H_{22}O_{22}$, would leave only carbon, C_{25} ; but this final result never occurs in nature under ordinary circumstances, because the excess of carbon holds the last portions of hydrogen with an increasing affinity as the amount of hydrogen diminishes.

It is probable, however, that the decay of lignine, in certain circumstances, may proceed to this extreme point; and if the carbon should be separated in a liquid, or in such a situation as to allow the particles to arrange themselves freely, it might crystallize, and thus yield the diamond. At all events, no other means are known by which diamonds can have been produced; and the recent discovery of the skeletons of organized tissues in the ashes of the diamond, which are the ashes of impurities enclosed in the crystals, has greatly added to the probability of this view of the origin of the diamond.

When wood is decomposed by the action of water in the absence of air, the process is properly termed *Mouldering*, to distinguish it from *eremacausis* or decay, in which oxygen is the active agent. In mouldering oxygen is not, it is true, entirely excluded; but its access is limited, and the results are different. The elements of water, along with some oxygen, are taken up, and carbonic acid escapes. Thus, when oak wood was decomposed by lying under water, a white mouldered matter was formed, containing $C_{33}H_{27}O_{24}$. This is derived from oak wood, $C_{36}H_{22}O_{22}$, by the addition of $5HO + O_3$, and the subtraction of $3CO_2$. Mouldered beech yielded $C_{33}H_{25}O_{24}$, which may be accounted for in a similar way.

Wood Coal, or *Brown Coal*, has been produced by a similar action. A pure specimen of wood coal from Laubach contained $C_{33}H_{21}O_{16}$; that is, a greater proportion of carbon and hydrogen, and a smaller proportion of oxygen, than wood.

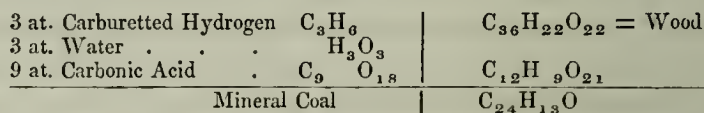
If wood were to lose 3 at. of carbonic acid and 1 at. of hydrogen, such a wood coal would be the result:



Another specimen, from Ringkühl, contained $C_{32}H_{15}O_9$, and differs from wood by 4 at. carbonic acid, 5 at. water, and 2 at. hydrogen.

A specimen of wood which had been long kept in the boiler of a steam-engine acquired the appearance of wood coal, and had the same composition. In the formation of wood coal the essential change seems to be the separation of carbonic acid from its elements, while a portion of hydrogen is removed by oxidation, owing to the limited access of air. The separation of carbonic acid seems still to go on even in the deepest beds of brown coal, and is the source of the acidulous springs found near such beds, and also of choke-damp in mines. When near the surface the proportion of hydrogen in wood coal is always less, owing to the action of the air, by the oxygen of which the hydrogen is removed.

Mineral Coal appears to be produced by a long-continued decomposition of wood or of wood coal, by which carbonic acid, water, and carburetted hydrogen are separated. Splint coal, and cannel coal, according to Richardson and Regnault, are both $C_{24}H_{13}O$, which may be thus derived from wood:—



Caking coal is $C_{20}H_9O$, or cannel coal *minus* olefiant gas, C_4H_4 . (Liebig.)

This explains the occurrence of fire-damp, or carburetted hydrogen, in coal-mines; whereas, in mines of wood coal, carbonic acid, or choke-damp, alone occurs. The occurrence of fire-damp proves that changes are constantly occurring in the beds of coal. When the whole of the hydrogen is removed in the form of carburetted hydrogen, the residue must be anthracite, which is nearly pure carbon.

Besides carbonic acid and light carburetted hydrogen, fire-damp, according to Bischoff, contains olefiant gas and nitrogen; the latter probably derived from the atmospheric air, although most specimens of coal contain nitrogen originally derived from the juices of the wood.

Some varieties of coal contain oily and resinous matters; and in some cases an oil, like oil of turpentine, may be obtained by distilling the coal with water. (Reichenbach.) It is possible that these oils and naphtha may be formed out of the elements of the carbonic acid and carburetted hydrogen separated from the wood during its conversion into coal; but if the wood have been originally pines, then the resin and oil of turpentine may have been originally present in it.

On the whole, the production of wood coal and mineral coal may be considered, not as a case of *eremacausis*, but as a process to which oxygen is not essential, and in which the elements present group themselves into new arrangements, in a manner somewhat analogous to what occurs in fermentation.

The brown acids discovered by Berzelius in certain mineral waters, and called by him *Crenic* and *Apocrenic* acids, appear to be modifications of humus, and are no doubt derived from the decay of vegetable matter.

PRODUCTS OF THE ACTION OF HEAT ON WOOD AND COAL.

When wood is heated in close vessels a variety of products are formed, some of which are solid, some liquid, and others gaseous. The gaseous products are chiefly carburetted hydrogen.

The liquid products separate into two portions, of which one is watery and acid, the other composed of tar and oily liquids. The watery portion contains much water and acetic or pyroligneous acid, pyroxylic spirit or hydrated oxide of methyle, and a good deal of the oily matters dissolved. The tar and oil contain a variety of new compounds, all combustible, and composed either of carbon and hydrogen, or of carbon, hydrogen, and a little oxygen.

The solid products are, charcoal left in the retort, and certain crystalline volatile compounds, which are found dissolved in the oil of tar. Of these, paraffine and naphthaline are carbo-hydrogens, while pyroxanthine contains also oxygen.

Having already described the gaseous carbo-hydrogens, pyroligneous acid, and pyroxylic spirit, we shall now give a brief account of the remaining products found in wood tar.

Eupion.—Discovered by Reichenbach. It is said by some to have the formula C_5H_6 ; by others, to be isomeric with olefiant gas. It may be obtained by repeated rectifications of oil of tar; but, as strong acids and alkalies were used in its purification, there is some reason to think, that, as finally obtained, it is a product of the decomposition of some other oil.

It is a very limpid, mobile, colourless fluid, of sp. gr. 0.655, which has a fragrant odour, and burns with a clear luminous flame. According to Reichenbach, it boils at a very low temperature, not above 100° F.; but in the experiments of others so volatile a liquid has not occurred. It is not altered by potassium, iodine, acids, or alkalies.

It appears that no other chemist has succeeded in obtaining eupion with precisely the characters ascribed to it by Reichenbach, and each experimenter has obtained a different modification of it. All these liquids, however, have a similar composition, which is either isomeric with olefiant gas, or very nearly so.

Creosote.—Formula, $C_{14}H_9O_2$ (Ettling); $C_{14}H_8O_2$ (Deville). This is the antiseptic principle of wood smoke, pyroligneous acid, and tar; and gives the smoked flavour to meat cured by smoke or pyroligneous acid. It is purified by repeated distillations, and by combination with potash, the process being very tedious. (Reichenbach.) It is an oily, colourless, highly refracting liquid, of sp. gr. 1.037, boiling at 397.4°, and burning with a smoky flame. It has a burning taste, and a strong smell of wood smoke, or rather of peat smoke. It combines with 80 parts of water, and is very soluble in acetic acid and alcohol. It also combines with potash, forming an oily anhydrous compound, and a hydrated one which crystallizes. When acted on by chlorate of potash and hydrochloric acid it yields chloranile, and with nitric acid it yields nitrophenisic and nitrophenesic acids. These facts indicate a close connexion with the series of phenyle. (See Carbolic Acid.)

Creosote possesses remarkable antiseptic properties; meat steeped in its aqueous solution may be preserved for a long period, and acquires a delicate smoked flavour, if the creosote be pure. This property appears to depend upon its action on albumen, which it instantly coagulates, and renders unsusceptible of putrefaction. Its name is derived from *κρεας*, flesh, and *σωζω*, I preserve. It dissolves a large number of organic substances, especially resins, gum-resins, and colouring matters.

As a remedy, creosote is very valuable. In the pure state, in that of ointment, or in the aqueous solution, it may be applied with the most decided benefit to almost all ulcers, wounds, and cutaneous affections. It promotes healing, and is very manageable. Internally it has been found very beneficial in cases of obstinate vomiting; but the dose must be carefully regulated, as it is poisonous in a certain quantity. One or two drops in a cup of water may be safely tried. Its solution is a very valuable styptic, and checks bleeding from wounds and cuts, probably by coagulating the blood, and thus closing the wounded vessel. In cases of toothache arising from a decayed tooth, the application of

pure creosote to the hollow, so as to touch the diseased nerve, is seldom known to fail in instantly removing the pain, and is often followed by a long exemption from suffering. Care must be taken not to swallow it, nor even to allow it to escape into the mouth, as it produces excoriation in the latter case. In toothache it probably acts by coagulating the secretions, and thus protecting the nerve from the atmosphere; but it certainly diminishes inflammation in ulcers when applied to them. The inhalation of its vapour has been recommended in consumption with ulceration of the lungs, and it will probably afford relief.

For the introduction of this valuable remedy we are indebted to Dr. Reichenbach, its discoverer. It may be added, that the editor has applied it successfully to external and cutaneous affections in horses and dogs; and that it is a valuable application to sheep, as it destroys the insects that infest them, without soiling the wool, as tar does, when used for the same purpose. It is used in the form of ointment.

Picamar (in pice amarum) is a bitter oil, also discovered in tar by Reichenbach. Its sp. gr. is 1.10, and it boils at 518° . It forms crystalline compounds with alkalies, but does not neutralize them. It requires further investigation.

Capnomor (from καπνος, smoke, and μοιρα, a part,) is another oily fluid, discovered in tar by Reichenbach. It is little known.

Carbolic Acid. *Syn. Hydrated Oxide of Phenyle.*—This acid was first discovered by Runge in coal tar, and subsequently studied and analyzed by Laurent. Its formula is $C_{12}H_6O_2 = C_{12}H_5O, HO$.

It is extracted by potash from that portion of the oil of coal tar which distils between 300° and 400° . On the addition of an acid to the alkaline solution, impure carbolic acid separates, which is purified by rectification with a little solid potash.

Pure carbolic acid generally appears as an oily liquid, colourless, and of high refractive power; but it is also obtained, either by rapid evaporation of its solution in ether, or by means of chloride of calcium, in the form of prismatic crystals, which, however, frequently assume the liquid form without any obvious cause, even at temperatures considerably below that at which the crystals had been formed. The composition of the liquid and that of the crystals are identical. Carbolic acid in the liquid form has the sp. gr. 1.062 to 1.065. When in crystals it melts at 94° ; but, as already stated, is often liquid at ordinary temperatures. It boils at 368° . It has a very strong and peculiar smell, so closely allied to that of creosote, if not identical with it, that it is difficult to suppose them to be distinct substances. In fact, except that creosote has the sp. gr. 1.037, and boils at 397° , and that it does not crystallize, there is hardly any difference in their properties. Both are powerfully

antiseptic and poisonous; both coagulate albumen; and we cannot doubt, that, since their origin is the same, (creosote being more characteristic of wood tar and carbolic acid of coal tar,) they are either essentially the same substance, or very closely allied in constitution. The composition and formula of carbolic acid may be considered as ascertained; but those of creosote are still involved in some doubt, although its composition in 100 parts differs but little from that of carbolic acid. Both substances combine with bases; but the salts of carbolic acid are more easily formed and more permanent than those of creosote. Lastly, the products of the action of nitric acid, and of a mixture of chlorate of potash and hydrochloric acid, on carbolic acid are in many respects the same as in the case of creosote. On the whole, therefore, it may be concluded either that creosote is impure carbolic acid, or a compound of that acid with another oily compound of nearly the same composition, and probably of basic properties.

When a splinter of fir wood is moistened with carbolic acid, and afterwards with moderately strong nitric acid, it becomes first of a deep blue colour, and afterwards brown.

By the action of chlorine and bromine carbolic acid, or hydrate of phenyle, is converted into acids, derived from carbolic acid by substitution. Nitric acid produces a similar series of derived acids, and sulphuric acid forms a coupled acid.

According to Laurent, all these compounds may be referred to the radical phenyle, $C_{12}H_5$, which is unknown in the separate state. To the same series may also be referred aniline and its derivatives. The starting point, or nucleus of the series, is considered by Laurent to be the carbo-hydrogen $C_{12}H_6$ or benzole, which he calls *phène*. The following table exhibits the views of Laurent as to this series of compounds.

Phène (Benzole)		$C_{12}H_5, H = C_{12}H_6$
Phenyle (unknown)		$C_{12}H_5$
Oxide of Phenyle (unknown)		$C_{12}H_5, O$
Hydrated Oxide of Phenyle (Carbolic Acid)		$C_{12}H_5, O, HO$
Chlorophenetic Acid		$C_{12} \left\{ \begin{array}{l} H_3 \\ Cl_2 \end{array} \right\} O, HO$
Chlorophenetic Acid (Chlorindoptenic Acid)		$C_{12} \left\{ \begin{array}{l} H_2 \\ Cl_3 \end{array} \right\} O, HO$
Chlorophenetic Acid (Chlorinised Chlorindoptenic Acid)		$C_{12}Cl_5, O, HO$
Bromophenetic Acid		$C_{12} \left\{ \begin{array}{l} H_2 \\ Br_3 \end{array} \right\} O, HO$
Nitrophenetic Acid		$C_{12} \left\{ \begin{array}{l} H_3 \\ 2NO_4 \end{array} \right\} O, HO$
Nitrophenetic Acid (Nitropicric Acid)		$C_{12} \left\{ \begin{array}{l} H_2 \\ 3NO_4 \end{array} \right\} O, HO$
Phenylamide (Aniline, Amaphenase)		$C_{12}H_5, Ad = C_{12}H_7, N$
Sulphophenetic Acid		$C_{12}H_5, O, HO + 2SO_3$

It is obvious from the above formula that the series of phenyle is connected with those of indigo and of salicycle, both of which, by the

action of nitric acid, yield nitropicric acid. This relation is further demonstrated by the fact that aniline, which in composition is the amide of the phenyle series, and occurs in coal tar along with carbolic acid, is easily obtained both from the indigo series and that of salicylc. The same remark applies to the series of benzole, even if we regard it as a separate series from that of phenyle, for aniline may be formed from nitrobenzide. Lastly, the derivatives of indigo, of salicylc, and of phenyle, all yield chloranile when acted on by chlorate of potash and hydrochloric acid.

Most of the substances in the above table have been already described, and the others are chiefly interesting from their composition. We shall not, therefore, enter into details concerning them.

Of *Rosolic Acid*, *Brunolic Acid*, and *Pyrrrole*, described by Runge as existing in coal tar, little or nothing is known. The latter body is basic, and two other basic oils, also discovered by Runge in coal tar, namely, kyanole (aniline), and leucole (leucoline or quinoline), have been already described among the artificial organic bases.

Pittacal (from *πίττα*, pitch, and *καλός*, beautiful) is a solid of a fine indigo-blue colour, assuming, when its surface is polished, the lustre of gold, which was obtained by Reichenbach from the action of baryta on a certain portion of the oil of tar. It is probably a product of the decomposition of some other substance by the baryta. It is coloured red by acids, and the colour restored by alkalies. It is insoluble in water, but may be suspended so as to pass through a filter. It would probably be available as a dye, if it could be procured easily; but Reichenbach has not yet published the process by which it is obtained. It is certain that baryta-water develops a blue colour in some specimens of oil of tar.

Cedrivet is another solid compound, also discovered by Reichenbach in tar. It is volatile, and forms a network of red crystals, but has hardly been studied.

Pyroxanthine.—This is a volatile crystalline solid, first observed by Scanlan in the crude pyroligneous spirit. When this is rectified with lime, the lime becomes dark brown; and when this coloured mass is acted on by hydrochloric acid, there is left undissolved a dark brown matter, which is a mixture of pyroxanthine and a resinous matter. The mass is boiled with hot alcohol, which, on cooling, deposits the pyroxanthine in crystals, which are purified by recrystallization. They are of an intense yellow colour, fusible, and volatile in a current of air, or with the vapour of other substances, but partly decomposed when heated alone in a dry tube. Pyroxanthine dissolves in sulphuric acid with a deep bluish-red, and in strong hydrochloric acid with a splendid pur-

ple colour, which soon passes to dark brown. Gregory found its composition to be very nearly $C_{21}H_9O_4$; but, as it forms no definite compounds, he could not control the analysis.

Paraffine, (from *parum* and *affinis*, because it is a highly indifferent compound.)—Discovered in tar by Reichenbach. It is also found in the products of the distillation of wax, (Ettling,) and in the petroleum of Rangoon. (Christison; Gregory.) Formula, CH , or some multiple of this?. Lewy has lately deduced from his experiments, and especially from the action of chlorine on paraffine, the formula $C_{24}H_{25}$.

It is a white fusible solid, resembling wax, and may be obtained from its solution in hot ether in shining scales. It may be distilled unchanged. Sp. gr. 0.870. It burns with a clear white flame, like wax. It is acted on by chlorine and by anhydrous sulphuric acid, but the reactions are not yet fully understood.

Naphthaline.—According to Reichenbach, naphthaline occurs among the products of the distillation of wood; but, as it is more characteristic of coal tar, we shall describe it as a product of the distillation of coal.

When coal is distilled it yields, besides coke, coal gas, a mixture of light carburetted hydrogen, olefiant gas, and the vapours of several volatile carbo-hydrogens, also a watery liquid containing ammonia and hydrocyanic acid; and, finally, tar and oil, containing most of the ingredients of wood tar, with a large proportion of naphthaline.

The formula of naphthaline is $C_{20}H_8$. It crystallizes from the oil of coal tar after it has been rectified, and is purified by crystallization from alcohol. It forms shining plates, of a strong and peculiar odour, volatile, fusible at 176° , boiling at 423° . It burns with a smoky flame.

The action of chlorine, bromine, nitric acid, and sulphuric acid on naphthaline gives rise to a large number of very remarkable compounds, which have been studied with singular perseverance by Laurent, and have furnished the most striking illustrations of his doctrine of substitutions, as now understood and pretty generally admitted. Our space will not permit us to describe in detail the modes of formation and characters of these compounds, which indeed are far more interesting from their bearing on theory than from their individual properties. We shall therefore endeavour to give a brief but comprehensive view of the derivatives of naphthaline, considered as products of substitution. The original papers of Laurent are scattered in different journals, and no connected account of them has appeared. This must be our excuse for the imperfections of the following summary.

In order to understand the views now to be explained concerning the derivatives of naphthaline, it is necessary to bear in mind that naphtha-

line, $C_{20}H_8$, is considered as a type, in which any one or more of the 8 eq. of hydrogen may be replaced by chlorine, bromine, or nitrous acid equivalent for equivalent, the type continuing unaltered. The nomenclature proposed by Laurent for these compounds is simple and ingenious, and aids the memory in retaining the composition of the different compounds. It is founded on the principle of using the five vowels, in their natural order, in the last syllable of the name, to indicate the number of atoms replaced, and prefixing a syllable to signify the nature of the replacing substance. Thus, the compound $C_{20}(H_7Cl)$, in which 1 eq. of hydrogen is replaced by chlorine, is called *chlonaphtase*; the compound $C_{20}(H_7Br)$ is *bronaphtase*; $C_{20}(H_6Cl_2)$ is *chlonaphtese*; $C_{20}(H_5Cl_3)$ is *chlonaphtise*, and so on. When we go further than 5 atoms replaced, in which case the vowel *u* is employed, as in $C_{20}(H_3Cl_5)$, *chlonaphtuse*, we return to *a*, adding a syllable to the name, as in $C_{20}(H_2Cl_6)$, which is *chlonaphtalase*; $C_{20}(HCl_7)$, which is *chlonaphtalese*; and, finally, $C_{20}Cl_8$, which is *chlonaphtalise*. The same rules apply to compounds in which nitrous acid, NO_4 , is the replacing substance, so that we have (NO_4 being, for brevity, represented by X) $C_{20}(H_7X)$, *nitronaphtase*; $C_{20}(H_6X_2)$, *nitronaphtese*, and so on. The artificial base, naphthalidine, $C_{20}H_9N$, may be viewed as naphthaline in which 1 eq. of hydrogen is replaced by one eq. of amide, $C_{20}\left\{\begin{smallmatrix} H_7 \\ Ad \end{smallmatrix}\right\}$; and may be named *amanaphtase*, just as aniline is amaphenase.

Where hydrogen is replaced partly by chlorine and partly by bromine, this is also expressed in the name. Thus, $C_{20}(H_4Cl_4)$ is *chlonaphtose*, and $C_{20}(H_4Cl_3Br)$ is *bromachlonaphtose*, or *chloribronaphtose*, the termination *ose* implying that 4 eq. of hydrogen have been replaced, while the prefixes *broma* and *chlori* indicate that 1 eq. of bromine and 3 of chlorine have replaced them. The same principle of nomenclature is applied in all analogous cases of substitution by Laurent, and we have already used it in describing other series, as, for example, the series of phenyle, in which we have chlorophenesic and nitrophenesic acids, &c.

The first effect of the action of chlorine on naphthaline is to produce two compounds, the *chloride of naphthaline*, $C_{20}H_8 + Cl_4$, and the *subchloride of naphthaline*, $C_{20}H_8 + Cl_2$. The former is a crystalline solid, best purified by means of hot oil of petroleum, which deposits it in crystals on cooling. The latter is an oily liquid. The action of bromine on naphthaline does not yield a bromide, but gives rise at once to bronaphtase.

Chlonaphtase, $C_{20}(H_7Cl)$, is formed when the subchloride is acted on by an alcoholic solution of potash. It is an oily liquid, and as yet is not known to exist in any other isomeric modification, although, as we

shall see under chlonaphtese, the existence of such modifications is highly probable. We have already seen that there are two isomeric forms of the compound *amaphenase* (phenamide), namely, aniline and picoline, and it is probable that the relation between them is the same as that which would subsist between two forms of chlonaphtase.

Bronaphtase, $C_{20}(H_7Br)$, is obtained by the action of bromine on naphthaline, avoiding excess of either substance. It is an oily liquid, and is only known in one form. It is decomposed by chlorine and by bromine; the latter converting it into bronaphtese, and the products of the action of bromine on bronaphtese.

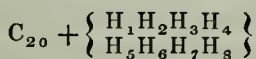
Chlonaphtese, $C_{20}(H_6Cl_2)$, occurs in no less than seven distinct isomeric forms. These are distinguished, according to Laurent, as the modifications *a*, *c*, *ad*, *e*, *f*, *x*, and *y*, but it does not appear on what principle the distinguishing letters are chosen. The modifications or forms, *a*, *c*, *f*, and *x* of chlonaphtese are all formed when chloride of N (N = naphthaline) is distilled; the forms *ad* and *e* are obtained by boiling chloride of N with an alcoholic solution of potash; and the form *y* is obtained by the action of chlorine on nitronaphtese. All of them are crystallizable, except *a* and *x*, which are liquid.

The solid forms of chlonaphtese have each a different melting-point, and all differ in volatility; they differ, further, in the results of their decomposition by chlorine or bromine; and those which crystallize differ in crystalline form. Now, since they all have the same composition, we must either suppose that they differ in the absolute amount of their elements, that is, in atomic weight, one being double, another triple, and so on, of the simplest; or we must adopt the much more probable view, that, in each of these forms, it is a different pair of molecules of hydrogen which has undergone replacement. In this view, it is not a matter of indifference which molecule of hydrogen is replaced by chlorine; on the contrary, the properties of the compound depend on the particular molecules of hydrogen which are replaced. If this be admitted, it follows that in a compound body, such as naphthaline, the chemical characters must depend on the relative position of the elementary molecules in the complex molecule of the compound, or, in other words, on the arrangement of the molecules, even more than they do on the properties of those elementary molecules, or their place in the electro-chemical arrangement.

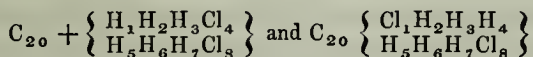
Viewing naphthaline as a type, the simplest molecule of that body is formed of 20 equivalent molecules of carbon and 8 of hydrogen. Now, we must suppose that these 8 molecules of hydrogen are arranged in some definite and regular manner, with reference to the 20 molecules of carbon; and that, if this arrangement be subverted, the compound is

destroyed. On this view, it is easy to perceive that any one or more of these may be replaced by a molecule of another element, without destroying the type, provided the arrangement continue as before. And if the molecules of hydrogen were replaced by those of a body analogous to it in properties, we should consider this result quite natural; as much so as the fact that when the sodium of common salt is replaced by potassium, or its chlorine by bromine, the resulting compound in both cases is very similar to common salt, and obviously belongs to the same type. But in the kind of substitution now under consideration we have hydrogen replaced by another element, which is not only not analogous to it, but is generally found opposed to it; chlorine, for example, being as strongly negative as hydrogen is positive. Yet, in the present and similar cases, the type is as little affected by the substitution of chlorine for hydrogen as that of common salt is by the substitution of potassium for sodium. In short, chlorine, when replacing hydrogen in the way now explained, appears to lose all its negative energy, and even to acquire the positive character of hydrogen. Now this can only be accounted for, in the present state of our knowledge, by supposing that in compounds of this class the position or arrangement of the molecules is of more importance, in reference to the properties of the compound, than their chemical or electrical character.

If we consider the facts already stated with regard to the different forms of chlonaphtese, we shall see that they greatly fortify this view. For, supposing the molecules of hydrogen in naphthaline to be numbered, and each to have its own fixed place in reference to the carbon, we can then understand how the different forms of chlonaphtese may be produced. Let us represent naphthaline as follows:—



the numbers being attached to distinguish the molecules of hydrogen; and we can then represent two of the varieties of chlonaphtese in the following manner:—



The former of these may be chlonaphtese α , the latter chlonaphtese x . It is evident that in each 2 eq. of hydrogen are replaced by chlorine; that in each a different pair of molecules is so replaced; and that, if each molecule of hydrogen have a fixed position in the compound atom, these two compounds may easily have different properties, although still, like chloride of potassium and chloride of sodium, or like potash-alum and ammonia-alum, belonging to the same type. The other varieties of chlonaphtese may be expressed in a similar way.

In naphthaline the character of the type is that it consists of 20 eq. of carbon and 8 of hydrogen, or chlorine, or bromine, or nitrous acid, or 8 eq., some of which are hydrogen, some chlorine, some bromine, and some nitrous acid, provided always the characteristic arrangement of the type naphthaline be preserved.

It is obvious that, theoretically, the number of modifications or forms of any given type must be very great. Naphthaline, for example, is the type, and chlonaphtase, chlonaphtese, bronaphtise, nitronaphtose, &c., are what may be called subtypes of the type naphthaline. Supposing each of the 8 eq. of hydrogen to be capable of successive replacement by chlorine, we have eight subtypes in which chlorine is the replacing body, and, of course, as many with bromine and with nitrous acid, besides other possible substitutes. Confining our attention, for the present, to these three replacing bodies, we have twenty-four subtypes.

Now let us take the first chlorine subtype, chlonaphtase, it is equally obvious, from what has been stated, that this may exist in eight distinct forms, according as the one molecule of hydrogen replaced by chlorine is molecule No. 1, 2, 3, 4, 5, 6, 7, or 8. Bronaphtase and nitronaphtase may also exhibit each 8 forms, on the same principle. Hitherto only one form of each of these three subtypes is known; but, in the analogous case of amaphenase, two forms, aniline and picoline, are already known; and in the case of the next subtype, chlonaphtese, the case is very different.

The subtype chlonaphtese, as has been shewn, may yield different modifications; but, as there are here 2 eq. of hydrogen replaced, it is evident that there may exist as many forms of chlonaphtese as there exist different pairs of molecules in 8. In the two examples above given the pairs replaced were the pairs 4 and 8 and 1 and 8. But eight numbers yield twenty-eight distinct pairs, and consequently there may exist twenty-eight forms of chlonaphtese. Of these, as we have seen, seven are already known.

We cannot here enter into details concerning the properties of the seven forms of chlonaphtese, which are all more or less analogous to those of the type, naphthaline, from which they are derived; but it is important to lay before the reader, as has now been done, a general view of the doctrine of types and substitutions as applied to these remarkable compounds. It will be remembered that in other cases, such as chloracetic acid, chlorophenisic acid, chloraniline, and chlorisatine, we have seen that hydrogen may be replaced by chlorine without altering the type or general chemical characters of the compound, whether it be acid, basic, or indifferent.

It cannot be doubted that the further study of this class of phenomena will shed light on the obscure subject of the molecular arrangement of bodies. We have already been enabled to trace a connexion between the composition of bodies and certain chemical and physical characters, such as acidity, basicity, density, volatility, and crystalline form, and we now perceive a prospect of connecting the chemical properties of compounds with their molecular arrangement. It is conceivable that a time may come when we shall be able, merely from an accurate study of the external physical and the chemical characters of a compound, without analyzing it, to infer its composition; and in like manner to predict, from their theoretical composition, the properties of compounds yet unknown.

Bronaphtese, $C_{20}(H_6Br_2)$, is readily obtained by the action of bromine on naphthaline or on bronaphtase. It is a crystalline solid, apparently isomorphous with chlonaphtese *c*. It forms several compounds with bromine. Only one form of bronaphtese is yet known.

Chlonaphtise, $C_{20}(H_5Cl_3)$, occurs in six different forms. The number of possible permutations in this subtype is, of course, much greater than in the preceding, amounting to fifty-six. Laurent distinguishes the different modifications as *chlonaphtise*, *a*, *ac*, *c*, *g*, *d*, and *ad*. They all crystallize. They are obtained by different methods, and from different substances, as, from chloride of chlonaphtase, chlonaphtese *ad*, and the double chloride of naphthaline and chlonaphtase, by the action of chlorine, of an alcoholic solution of potash, or of heat, in a manner analogous to what was stated under chlonaphtase.

Bronaphtise, $C_{20}(H_5Br_3)$, is only known in one form, which is crystalline, and is formed when heat is applied to the bromide of bronaphtise, a product of the action of bromine on naphthaline or on bronaphtase.

Chlonaphtose, $C_{20}(H_4Cl_4)$, occurs in four isomeric forms out of a very large number which are evidently possible. All of them are crystallizable. Their mode of formation is analogous to that of the different varieties of chlonaphtese and chlonaphtise.

Bronaphtose, $C_{20}(H_4Br_4)$, is known in two forms, *a* and *b*, both of which are crystalline.

Chlonaphtuse, $C_{20}(H_3Cl_5)$, and *Bronaphtuse*, $C_{20}(H_3Br_5)$, are not yet known.

Chlonaphtalase, $C_{20}(H_2Cl_6)$, is formed by the action of chlorine on chlonaphtise *a*, and crystallizes in soft flexible prisms.

Chlonaphtalese, $C_{20}(HCl_7)$, is unknown.

Chlonaphtalise, $C_{20}Cl_8$, in which the whole of the hydrogen is replaced by chlorine, is obtained by the continued action of chlorine on

chlonaftise α , and is a crystalline solid. Laurent conceives it to correspond to the modifications c of chlonaftese and chlonaftise, probably on account of the form of its crystals; and for a similar reason he considers the only known form of chlonaftalase to correspond to the modifications α . In the case of chlonaftalise, however, it is evident, that, if different modifications can occur, and it does not at present appear to be proved that this is the case, these modifications must depend on some other principle than that already explained, which applies only to the cases in which both chlorine and hydrogen are concerned. It is not easy to see how chlonaftalise should admit of different modifications any more than naphthaline itself; nor can we ascertain exactly the views of Laurent on these points, until he shall publish a connected account of his researches. It is indeed conceivable that there might be different forms of chlonaftalise, according to the order in which the molecules of hydrogen have been replaced. Thus, if we take two varieties of chlonaftese, in one of which the molecules 1 and 8, and in the other the molecules 4 and 8, have been replaced by chlorine, and if we convert these into two forms of chlonaftose, in one of which the molecules 3 and 5, and in the other the molecules 2 and 6, are replaced; and if, finally, we convert these two forms of chlonaftose into chlonaftalise, it may be said that the eight molecules of hydrogen have been replaced in a different order of succession in the two compounds, so that one of them is a derivative of chlonaftose α , and the other of chlonaftose β . This, we say, is conceivable; but we have as yet no evidence in favour of its actual occurrence. Were the fact so, then the possible number of forms of chlonaftase, chlonaftese, &c. would be enormously increased, since in each of these subtypes the same principle, if true, would apply. But, until we shall obtain proof of the existence of more than one form of chlonaftalise or of naphthaline, it is not necessary to adopt any such hypothesis.

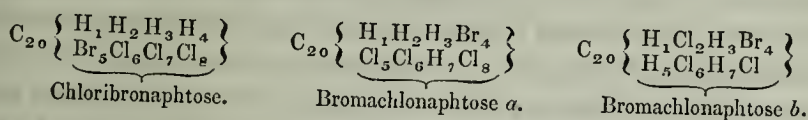
Besides the compounds above enumerated, there are several in which the hydrogen of naphthaline is replaced partly by bromine, partly by chlorine.

Chlorebronaftise, $C_{20}(H_5Cl_2Br)$, is a crystalline solid, corresponding to chlonaftise α .

Chlorebronaftose, $C_{20}(H_4Cl_2Br)$, is formed by the action of bromine on chlonaftese f .

Chloribronaftose a, *Bromachlonaftose a*, and *Bromachlonaftose b*, are three isomeric compounds, the formula of which is $C_{20}(H_4Cl_3Br)$. The first is derived from chlonaftise α by the action of bromine, and therefore the chlorine is placed first in the name. The two others are formed by the action of chlorine on bronaftese, and on this account

the bromine is placed first in the name. All three are crystallizable. These compounds furnish additional arguments in favour of the influence of position or arrangement on the properties of the compound; for, while their formulæ are empirically identical, their properties are quite different, and we have even a proof in their mode of formation that this difference depends on the fact that in one of these compounds the four molecules of hydrogen replaced are not the same four as in the others. The first of the three is derived from ehlonaphtise, $C_{20}(H_5Cl_3)$, the two others from bronaphtese, $C_{20}(H_6Br_2)$; and from these facts we can draw no other conclusion than that the replaced molecules occupied different positions in the typic molecule. The difference of these three compounds may be illustrated as follows:—



Bromechlonaphtise b, $C_{20}(H_3Cl_3Br_2)$, is a crystalline solid, obtained by boiling chloride of bromechlonaphtise with an alcoholic solution of potash.

Chloribronaphtise, $C_{20}(H_3Cl_3Br_2)$, is isomeric with the preceding, is formed by the action of bromine on ehloride of naphthaline. It is also a crystalline solid.

In addition to the substances above-mentioned, there are a large number of compounds analogous to the ehlorides of naphthaline, and, like them, containing, in addition to the subtype, chlorine or bromine. Such compounds are *chloride of chlonaphtase*, which forms large and beautiful crystals, $Cl_4 + C_{20}(H_7Cl)$; *chloride of chlonaphtese*, $Cl_4 + C_{20}(H_6Cl_2)$, which occurs in three isomeric forms; *bromide of chlonaphtese*, *bromide of chlorabronaphtese*, *chloride of bromechlonaphtise*, and many more, almost all of which crystallize, but which we have only space to allude to.

From what has been said, it will be seen that the number of forms or varieties derivable from the type naphthaline by the action of ehlorine and bromine is very great, and that in a large proportion of these the type remains unchanged. If we consider that one subtype, such as chlonaphtase, may occur in eight forms; another, ehlonaphtese, in twenty-eight; chlonaphtise in fifty-six, and the remaining ehlorinized subtypes in a far greater number of different forms; that the corresponding brominized subtypes may present equally numerous modifications, and that each of these subtypes may be modified by the introduction of ehlorine or bromine, giving rise to such modified subtypes as chloribronaphtose, &c., each of which in its turn may exhibit an almost endless variety of forms, still included under the original type of naph-

thaline; we may form a faint conception of the infinite variety of which nature is capable, even when confined to the limits of a given type. And it must be remembered that the facts ascertained by Laurent are sufficient to demonstrate the actual existence of very numerous modifications of the type naphthaline, even should his views as to the explanation of these remarkable phenomena not be confirmed by future researches.

ACTION OF NITRIC ACID ON NAPHTHALINE.

Naphthaline, when acted on by nitric acid, gives rise to a series of compounds, in which the hydrogen is replaced by nitrous acid, NO_2 , equivalent for equivalent. The same general observations apply here as in the case of the action of chlorine and bromine, and the same principle of nomenclature is adopted. In representing these compounds, which we can only briefly enumerate, we shall use X to signify nitrous acid.

Nitronaphtase, (*syn. Nitronaphtalase*), $\text{C}_{20}(\text{H}_7\text{X})$, is best formed by causing nitrous acid to pass through melted naphthaline. It is purified by solution in alcohol, from which it crystallizes in long sulphur-yellow prisms, fusible at 110° . By chlorine it is decomposed, yielding chlonaphtose. Nitric acid converts it into nitronaphtese. When dissolved in alcohol, and subjected to the action of sulphuret of ammonium, it yields the artificial base *naphthalidine*. When nitronaphtase is gently heated with 10 parts of lime slightly moistened, it is decomposed, yielding a new compound in yellow crystals, which colours oil of vitriol deep blue, and might be taken for pyroxanthine, but for its insolubility in alcohol. The formula of this substance is $\text{C}_{20}\text{H}_7\text{O}$, and Laurent considers it as naphthaline in which 1 eq. of hydrogen is replaced by oxygen. If it be really so, this would indicate the existence of a series of products in which oxygen is the replacing body, a very remarkable fact, considering the high negative energy of oxygen. Laurent has named this substance *naphthalase* or *naphtease*.

Nitronaphtese, (*syn. Nitronaphtalese*), $\text{C}_{20}(\text{H}_6\text{X}_2)$, formed by the action of nitric acid on the preceding compound, is a crystalline powder, insoluble in water, sparingly soluble in alcohol, fusible at 365° . When boiled with tincture of potash it yields nitronaphtesic acid. By the action of sulphuret of ammonium on its alcoholic solution, it yields the artificial base *seminaphtalidine*.

Nitronaphtese is a crystalline compound, formed when naphthaline is added to a large excess of nitric acid. Its formation is accompanied by that of nitronaphtise. It has a pale yellow colour, and is very fusible, (melting in boiling alcohol,) and very soluble in ether. Its analysis indicates a composition intermediate between that of nitronaphtese and

that of nitronaphtise, and it would be considered merely as a mixture of these two in equivalent proportions, but for its much greater fusibility, and its solubility in ether, in which they are insoluble. Laurent gives the formula $C_{20}(H_{53}X_{23})$; but it is more probable that its true formula is the double of this, and that it is a *compound* of nitronaphtese and nitronaphtise, in which case it will be represented by the formula $C_{20}(H_6X_2) + C_{20}(H_5X_3)$.

Nitronaphtise, $C_{20}(H_5X_3)$, is formed along with the preceding body. It forms pale yellow rhomboidal plates, only fusible at 410° .

Nitronaphtale, $C_{19}H_5N_3O_{11}$, is a crystalline solid, obtained from the mother-liquid of all the preceding compounds by the further action of nitric acid. It melts at 420° . Its formula, if correct, would indicate that it is derived from nitronaphtise by the loss of 1 eq. of carbonic oxide; but, as that is not very probable, it may be conjectured that this substance, whose point of fusion is so near that of nitronaphtise, is really nitronaphtise in an impure state, possibly mixed with a little nitronaphtose, which would have the effect, in all probability, of raising its melting-point, and which would also diminish the amount of carbon.

Nitronaphtesie, nitronaphteisie and nitronaphtisie acids are brown substances, apparently resembling humic acid, formed by the action of boiling tincture of potash on nitronaphtese, nitronaphtise, and nitronaphtise. Their salts are brown, and do not crystallize, and the formulæ do not seem to be fully established. They may possibly be essentially one acid, and at all events do not belong to the original type, one of them, according to Laurent, containing 16, and another 12 eq. of carbon.

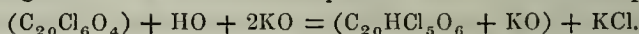
Oxide of Chloroxénaphthose, $O_2 + C_{20}(H_4Cl_2O_2)$, is formed when nitric acid acts on crystallized chloride of chlonaphthose. It is yellow and crystalline. It is converted, by boiling with tincture of potash, into chloranaphtisie acid, an acid which is also formed along with the oxide of chloroxénaphthose. The existence of this compound seems to favour the idea that there is a series of subtypes of naphthaline in which oxygen replaces hydrogen.

Chloranaphtisie Acid, $C_{20}H_5ClO_6$, or $C_{20}(H_5ClO_2) + O_4$, is formed from the preceding compound, as in the equation $C_{20} + (H_4Cl_2O_2) + HO + 2KO = KCl + KO(C_{20}H_5ClO_6)$. Taking the second of the two formulæ above given for this acid, it is an *oxide of chloroxénaphthose*, corresponding to the chlorides or bromides of naphthaline, or of chlonaphthose, or of bromechlonaphthose, &c., all of which contain 4 eq. of chlorine or bromine. In this view, the existence of this compound is a further instance of the existence of the series of subtypes above alluded to, in which hydrogen is replaced by oxygen. On the addition

of a stronger acid to the alkaline solution the new acid is separated, and forms yellow crystals, fusible at 392° . Its salts are generally insoluble, and of very fine colours, yellow, orange, red, and crimson. Its proper name, according to the rules of the nomenclature for these compounds, would seem to be chloroxénaphthistic acid $= C_{20}(H_5ClO_2) + O_4$.

Oxide of Chloroxenaphthalise, $O_2 + C_{20}(Cl_6O_2)$, is formed, with other compounds, when chlonaphtalese, $C_{20}(H_2Cl_6)$, is boiled with nitric acid, and crystallizes in golden-yellow scales.

Chloroxénaphtalesic Acid, $C_{20}HCl_5O_6$, or $C_{20}(HCl_5O_2) + O_4$, is formed from the preceding compound by the action of potash, which converts it into a fine carmine-red salt; and from this acids precipitate the new compound as a crystalline yellow powder. Its salts with ammonia and potash have a beautiful red colour. Its formation is perfectly analogous to that of chloranaphthistic acid, as above explained.



Phtalic Acid. Syn. Naphtalic Acid.—This acid, the formula of which is $C_{16}H_6O_8 = C_{16}H_4O_6 \cdot 2HO$, is formed by the action of nitric acid on chloride of naphthaline. It no longer belongs to the series of naphthaline; for which reason the name phtalic acid seems the preferable one. It forms radiated bundles of lamellar crystals, and yields with bases crystallizable salts. When distilled alone it loses water, and gives a sublimate of the anhydrous acid in fine needles. Heated with lime, it is resolved into 4 eq. of carbonic acid, and 1 eq. of phène (benzole). (Laurent; De Marignac.)

The acid phtalate of ammonia, $(C_{16}H_4O_6, HO, NH_4O)$, when heated, gives off 4 eq. of water, leaving *Phtalimide*, $(C_{16}H_5NO_4 = C_{16}H_4O_4, NH)$.

Phtalamide, $C_{16}H_6NO_5 = C_{16}H_4O_5, NH_2$, is formed when anhydrous phtalic acid is acted on by dry ammonia, 1 eq. of water being given off. Both this and the preceding compound are crystallizable, and both appear to form definite compounds with oxide of silver.

Nitraphtalic Acid, $C_{16}H_3NO_{10} \cdot 2HO$, is derived from phtalic acid by the substitution of 1 eq. NO_4 for 1 eq. hydrogen. It forms fine pale yellow crystals, which are resolved by heat into water and anhydrous acid, the latter appearing in fine white needles. The formula of the hydrated acid may be represented as follows, $C_{16}\left\{\begin{smallmatrix} H_3 \\ X \end{smallmatrix}\right\}O_6 \cdot 2HO$, which shews its relation to phtalic acid, $C_{16}H_4O_6 \cdot 2HO$.

Chlophthalisic Acid is an analogous product, in which 3 eq. of hydrogen in anhydrous phtalic acid ($C_{16}H_4O_6$) are replaced by chlorine. It is formed, along with chloroxénaphthose, when chlonaphthalase is boiled with nitric acid. It is crystallizable, and its formula is $C_{16}HCl_3O_6$.

ACTION OF SULPHURIC ACID ON NAPHTHALINE.

When oil of vitriol is made to dissolve as much naphthaline as it can by the aid of a gentle heat, the solution, when left exposed to the air, forms a semi-solid mass of a dirty purplish hue. This is dried by placing it on a porous tile, when it leaves a mass of scales, very soluble in water and alcohol, and consisting of two acids.

Hyposulphonaphthalic Acid.—The scales above mentioned are dissolved in water, and neutralized by carbonate of lead, which separates the free sulphuric acid as sulphate of lead, and forms soluble salts with the two new acids. One of them dissolves in alcohol, and, when decomposed by sulphuretted hydrogen, yields hyposulphonaphthalic acid. Its solution yields, on evaporation, the acid as a hard, crystalline, fusible mass, and of an acrid and bitter taste. Its formula is $C_{20}H_8S_2O_5 + HO$; and it appears, therefore, to be a coupled acid, consisting of hyposulphuric acid, coupled with naphthaline, which does not affect its saturating power.

Hyposulphonaphptic Acid ($C_{11}H_5S_2O_6 = C_{11}H_4S_2O_5, HO$) is contained in the lead salt insoluble in alcohol. Its salts are soluble, bitter, and not easily crystallizable. If it be a hydrated and coupled acid, containing hyposulphuric acid, the coupled substance is $C_{11}H_4$, a somewhat unlikely formula; and it is probable that this acid is not yet known in a state of purity. There is, indeed, reason to think, from the experiments of Berzelius and of Faraday, that a third acid is present along with these two; but it has not yet been isolated.

When anhydrous sulphuric acid is made to act on naphthaline with the aid of heat, a red liquid is formed. If the acid be in excess, there is produced, along with a little of the preceding acids, *hyposulphoglutinic acid*, which forms a glassy mass when dry, and when precipitated from its salts is thick and viscid. Its composition is unknown, and its salts do not crystallize.

If the naphthaline be in excess, there are formed two neutral compounds, *sulphonaphthaline*, $C_{20}H_8SO_2$?, a fusible crystalline solid; and *sulphonaphthalide*, $C_{24}H_{10}SO_2$?, a crystalline powder, fusible at 212° .

Anthracene. Syn. Paranaphthaline. $C_{30}H_{12}$.—This compound, polymeric with naphthaline, is also found in coal-tar. It melts at 356° , and boils at 392° , subliming in foliated crystals. When acted on by nitric acid it forms a series of products, in which hyponitrous acid is found combined with compounds derived from anthracene by the substitution of oxygen for hydrogen. Chlorine also acts on it, and will

probably be found to yield a series of chlorinized products, only one of which has been as yet obtained. Laurent alone has studied this subject, and the compounds formed by him are little known. We shall, therefore, subjoin a table of their names and composition.

Anthracene	.	.	$C_{30}H_{12}$
Hyponitrite of Anthracenase	.	.	$C_{30}H_{11}O + NO_3$ unknown
" Anthracenese	.	.	$C_{30}H_{10}O_2 + 2NO_3$
" Anthracenise	.	.	$C_{30}H_9O_3 + 3NO_3 + 3HO$
" Anthracenose	.	.	$C_{30}H_8O_4 + NO_3$
" Anthracenuse	.	.	$C_{30}H_7O_5 + NO_3 + HO$
Anthracenuse	.	.	$C_{30}H_7O_5$
Chloranthracenese	.	.	$C_{30}H_{10}Cl_2$

The circumstance that the third and fourth compounds in the table contain as many equivalents of hyponitrous acid as of oxygen, might lead us to suppose that they were really compounds in which nitrous acid (NO_4) was substituted for oxygen, in which case their names and formulæ would be ($X = NO_4$):—

Nitranthracenese	.	.	$C_{30}H_{10}X_2$
Terhydrate of Nitranthracenise	.	.	$C_{30}H_9X_3 + 3HO.$

It is possible, however, that their properties may indicate that the formulæ given in the table are correct.

Chrysène (C_3H or $C_{12}H_4$) and *Pyrène* ($C_{10}H_2$ or $C_{15}H_3$) are two crystalline solids, found in the last portions, which are the least volatile, of the rectification of coal-tar. Chrysène is yellow, and fusible at 455° . Pyrène is white, and more fusible. They are little known, but appear, by the experiments of Laurent, to yield with nitric acid compounds analogous to those of anthracène, such as hyponitrite of chrysenase, $C_{12}(H_3O) + NO_3$, and hyponitrite of pyrenase, $C_{15}(H_2O) + NO_3$. The former of these, when further acted on by nitric acid, yields the compound $C_{12}(H_{23}O_{13}) + NO_3$, or rather $C_{24}(H_5O_3) + 2NO_3$, which may be called *Hyponitrite of Chrysenase*.

Ampeline is an oil obtained by the distillation of bituminous schist, along with other oils. It has neither taste nor smell, and its composition is unknown. As oil of vitriol is used in its purification, it may be a product of the action of that acid on some of the original products of the distillation.

Ampelic Acid is formed by the action of nitric acid on that part of the oil of schist which distils at 300° . It is oily, and soluble in hot water, forming also soluble salts. Its composition is not known; but a similar oil from coal-tar was found to be $C_{14}H_6O_6$, which formula is isomeric with that of salicylic acid.

Pyroxanthine is a yellow volatile solid, found by Scanlan in crude pyroxylic spirit. When the spirit is rectified with lime, the pyroxan-

thine remains attached to the lime, along with much brown resinous matter. The lime is dissolved out by hydrochloric acid, and the dark-brown residue boiled with successive portions of alcohol. The first portions dissolve chiefly resin, and are very dark; but, after a few operations, the hot alcohol is found to have a strong yellow colour, and on cooling deposits pyroxanthine nearly pure. (Gregory.) It is purified by re-solution in alcohol, and forms fine orange-yellow needles, resembling nitropicrate of potash. They are insoluble in water, but dissolve in oil of vitriol with a deep blue, and in strong hydrochloric acid with a beautiful purplish-red colour. The analysis of pyroxanthine by Gregory and Apjohn yielded very nearly the formula $C_{21}H_9O_4$; but, as the substance forms no definite compounds, this formula could not be controlled, and must be considered doubtful. The naphthalase of Laurent, $C_{20}(H_7O)$, as described by him, resembles pyroxanthine in most of its external and chemical characters, and we might suppose them to be identical, were it not that naphthalase is said to be insoluble in alcohol, and that the composition differs, especially in the oxygen. As, however, the formula of pyroxanthine is doubtful, it is not improbable that it belongs to the series of naphthaline, and contains only 20 eq. of carbon.

Coal Naphtha is obtained by the rectification of coal-tar, and appears to be a mixture of various oils not yet fully investigated. It is important as being the solvent for caoutchouc, used in making waterproof cloth.

Petroleum and Naphtha.—In various parts of the world, as near the Caspian Sea, near the Tegernsee in Bavaria, at Amiano in Italy, at Neufchatel, and at Rangoon in Ava, an oily matter is found floating on water in pits dug in the earth or in springs. It is called petroleum, or rock oil. Some kinds are pale and very fluid, and consist chiefly of naphtha; others are dark and semi-solid at the ordinary temperature. These last, when distilled, yield first a colourless naphtha, and afterwards a quantity of paraffine. The purest naphtha has the sp. gr. 0.755, and its formula is said to be C_6H_5 . It is used for preserving potassium and sodium.

According to Reichenbach, coal, when distilled with water, yields a little oil, somewhat similar to petroleum.

It is not ascertained whether petroleum is formed by the action of heat on vegetable matter or coal, or by the decay of those substances taking place at considerable depths. Those kinds which contain paraffine may certainly be supposed to owe their origin to heat.

FOSSIL RESINS, WAX, BITUMEN, ETC.

Retinite or *Retinasphalt* is a fossil resin found in wood coal. It sometimes contains *retinic acid* ($C_{21}H_9O_3$). (Johnston.)

Hatchetine and *Scheererite* are two combustible fossil substances, also found in lignite or wood coal, and supposed to be carbo-hydrogens.

Middletonite is a fossil resin found in coal.

Ozokerite, or fossil wax, is found in large masses in the bituminous schist of Moldavia. It seems to contain paraffine.

Fichtelite is a fusible, volatile, and crystallizable solid, found in the remains of pine trees in the peat of the Fichtelgebirge. Its composition is $C_{20}H_{15}$, which is perhaps derived from oil of turpentine ($C_{20}H_{16}$), or from resin of turpentine ($C_{20}H_{16}O$).

Tekoretine ($C_{10}H_9$), *Phylloretine* (C_5H_3), *Xyloretine* ($C_{40}H_{33}O_4$), and *Boloretine* ($C_{40}H_{32} + 3HO$), are found in the remains of pine trees in the peat of Denmark. The two former are fusible, volatile, and crystallizable. Xyloretine, which has only 1 eq. of hydrogen more than sylic acid, is fusible and crystallizable, but is decomposed by heat. Boloretine is fusible, but does not crystallize.

Idrialine (C_3H , or perhaps $C_{21}H_7$) is a remarkable white and crystalline volatile carbo-hydrogen, found in the quicksilver ores of Idria. It colours oil of vitriol intensely blue, forming a coupled acid. Pelletier and Walther obtained, among the products of the distillation of amber, a white solid compound, to which they gave the name *succisterène*. As it has the same composition in 100 parts as idrialine, and also colours oil of vitriol blue, the two substances are probably identical.

Soot and *Lamp Black* are formed by the imperfect combustion of organic matter, and consist chiefly of carbon, mixed, in soot, with an acid resinous body, and with a humus-like substance, *asboline*, which contains nitrogen. Lamp black contains naphthaline in variable quantity, besides resinous and oily matters.

Asphaltum. Mineral Pitch. Pitch of Judæa.—These names are given to pitch-like substances found in various parts of the world, as near the Dead Sea, in Hanover, in North Africa, and in Trinidad. They generally contain a dark-coloured resin, a brilliant black substance called *Asphaltène* ($C_{20}H_{16}O_3$), and a liquid volatile oil, *petrolène* ($C_{20}H_{16}$), that is, of the composition of oil of turpentine. Asphaltum, or bitumen, as it is often called, is much used for waterproof cements, and, more recently, mixed with sand or other similar matters, for pavements and roofs.

INDIFFERENT COMPOUNDS, CONTAINING NITROGEN AND SULPHUR,
AND COMMON TO THE VEGETABLE AND ANIMAL KINGDOMS.

We have now to consider a very important class of compounds, originating in vegetables, but indispensable to the formation of the animal organism. They occur in three principal forms, namely, *Albumen*, *Fibrine*, and *Caseine*, besides several modifications of these.

The first important character of these bodies is, that they contain nitrogen, in the proportion of from 13 or 14 to 17 or 18 per cent. of the dried substance; sulphur, in the proportion of from $\frac{1}{2}$ to $2\frac{1}{2}$ per cent.; and a certain small, but altogether essential quantity of phosphates, chiefly earthy.

The next remarkable peculiarity of these compounds is, that they are nearly alike in composition, while they are perfectly distinct in properties. So closely do they approach each other in composition, that some chemists have deduced from their analyses the result, that, after deducting the phosphates or other mineral constituents, and the sulphur which they contain, which last is not in the form of sulphuric acid, the remaining elements are exactly in the same proportion in albumen, fibrine, and caseine, as well as in most of their modifications.

According to Mulder, when either of these substances is dissolved in a moderately strong solution of caustic potash with the aid of a gentle heat, the sulphur is detached from the rest of the combination, and the addition of acetic acid causes a gelatinous precipitate, which when dried is found to be free from sulphur, and to have in every case the same composition, represented by the formula $C_{40}H_{31}N_5O_{12}$.

Mulder conceived that this compound, which he called *Proteine*, was the basis of all these substances, and that the difference in their properties depended on the circumstance that the proteine in each was united with different proportions of sulphur (or, in some cases, of sulphur and phosphorus) and of salts. The following table will explain Mulder's views, as published in his latest work, "Versuch einer physiologischen Chemie:"—

Crystalline humour contains 15 eq. Proteine + 1 eq. Sulphur					
Caseine	"	10	"	"	+ 1 " "
Vegetable Gelatine	"	10	"	"	+ 2 " "
Albumen of Eggs	"	10	"	"	+ 1 " " + 1 eq. Phosphorus
Fibrine	"	10	"	"	+ 1 " " + 1 " "
Albumen of Blood	"	10	"	"	+ 2 " " + 1 " "

In this table the salts are omitted.

There are several circumstances favourable to this theory. In the first place, these compounds, while differing in many properties, yet

possess certain common characters, such as might be supposed to depend on the presence of a common ingredient, like proteine. All of them, for example, when acted on by potash, yield proteine, according to Mulder, and when the action is pushed further they all furnish the same products; they all dissolve, with the aid of heat, in strong hydrochloric acid, forming a solution of a deep purple colour, a property possessed also by proteine; and when dried at 212° they are hardly to be distinguished from each other in external characters.

But, on the other hand, there are many things not consistent with the theory of proteine. This theory, in the first place, assumes that, after deducting the sulphur, phosphorus, and salts, albumen, fibrine, caseine, &c. have exactly the same composition. Now, although the analyses of Mulder to a certain extent favour this idea, yet, if we examine those of other chemists, as well those made previously as those made since Mulder began to publish on the subject, we shall find that experiment is opposed to this conclusion. For example, the analyses of Gay-Lussac and Thénard, of Michaelis, of Vogel, and of Fellenberg, agree in this, that fibrine contains more nitrogen than albumen does.

Further, if the first action of potash, that which, according to Mulder, produces proteine, be such as he has described, we ought to obtain a quantity of proteine nearly equal to that of the original compound. But this is very far from being the case; for the amount of proteine obtained from albumen, fibrine, or caseine is variable, and always very small, indicating that other products, not yet examined, are formed at the same time.

Again, on Mulder's theory, proteine contains no sulphur; but recent researches have shewn that a compound free from sulphur cannot be obtained by Mulder's process.

Lastly, it appears, from the determinations recently made, with improved methods, by Laskowski, Rüling, Verdeil, Walther, Fleitmann, and others, that the amount of sulphur present in albumen, fibrine, caseine, &c. (which, for the sake of brevity, we shall in future call *albuminous substances*) is three or four times as great as it would be if Mulder's formulæ were correct; that fibrine differs in composition from albumen, although in Mulder's table they have the same formula; and that the albumen of eggs, instead of containing less sulphur than the albumen of blood, as in Mulder's table, contains more of that element.

Although it is evident from these considerations that the theory of Mulder has not that degree of support from experiment which is necessary to establish it, yet at the time when it appeared, and while the laborious researches of Mulder were supposed to have demonstrated the identity of composition (excluding sulphur, &c.) of the various albu-

minous compounds, this theory was generally received, and became, in fact, the basis of physiological chemistry. It explained in a plausible manner the identity of composition just mentioned, as well as the mutual convertibility of the albuminous compounds in the animal organism; and even chemists overlooked the inconsistency of giving to fibrine and albumen the same formula, on a theory which professed to explain difference of properties by difference of composition, as well as the improbability of the supposed difference in composition between bodies so nearly identical in properties as the albumen of blood and the albumen of eggs, while fibrine and albumen, bodies totally distinct, had the same composition.

The phenomena of isomerism and polymerism have made us familiar with examples of difference of properties with the same composition in 100 parts; but the albuminous compounds were not supposed to be isomeric, but were assumed to contain a common principle, proteine, united, in each case, to a small quantity of sulphur or phosphorus, and phosphates. It was also supposed, that, unless on this view, the ready convertibility, in the animal body, of fibrine, for example, into albumen and caseine, could not be accounted for. But, if we reflect on known phenomena, it will appear that the supposition of the existence of a common constituent, such as proteine, in the albuminous compounds, is not necessary to explain their mutual convertibility; and when to this consideration is added the fact that the identity of composition, deduced by Mulder from his experiments, does not, in all probability, really exist, it must be admitted that the theory of proteine, however apparently simple and attractive, is not, as yet, justified by facts.

The albuminous compounds, in general, are of a very complex nature, and, for many reasons, it is extremely difficult to determine with accuracy their composition. Their atomic weight is very high, and in such cases an error of small amount, especially in the hydrogen, may make a difference of several equivalents in the formula. Indeed, Liebig has shewn that the analyses of proteine agree even better with the formula $C_{49}H_{36}N_6O_{14}$, than with Mulder's formula $C_{40}H_{31}N_5O_{12}$. Again, the difficulty of purifying the albuminous compounds is so great, since none of them are either crystallizable or volatile, that we have no security for the purity of the compounds analyzed. Lastly, the proportion of sulphur is small, and in such compounds a small percentage of sulphur is very difficult to determine with accuracy, although the improved methods lately introduced have doubtless brought us nearer to the truth.

As to the presence of phosphorus in the albuminous compounds in any other form besides that of phosphates, this, although admitted by

Mulder in albumen and fibrine, is very doubtful, and certainly not established by any sufficient experiments.

On the whole, it appears that the composition of the albuminous compounds is not yet established so accurately as to permit us to infer their formulæ; and, since ultimate analysis alone can never enable us to do this, we must have recourse to the only other available method, that of studying the products of decomposition. We have seen in the case of salicine that the formula of that substance, which remained doubtful as long as we depended solely on ultimate analysis, was instantly fixed as soon as Piria discovered a mode of resolving it into two definite products. In like manner, we cannot expect to ascertain the true formulæ of the albuminous compounds till we shall have succeeded in resolving them into less complex substances, capable of being purified, and the absolute amount as well as the formulæ of which can be determined.

It is true that Mulder has described the decomposition of proteine compounds by potash, and has enumerated the products as follows:—

		C	H	N	O
2 eq. Leucine	. .	24	24	2	8
2 „ Protide	. .	26	18	2	8
2 „ Erythroprotide	. .	26	16	2	10
4 „ Ammonia	. .	—	12	4	—
2 „ Carbonic Acid	. .	2	—	—	4
1 „ Formic Acid	. .	2	1	—	3
2 eq. Proteine + 9 eq. Water		80	71	10	33

But this statement cannot be considered satisfactory; for protide and erythroprotide do not admit of purification, and give results so variable as to shew that they are mixtures. No formic acid is produced in the process, but other acids are, among which are oxalic, butyric, and valerianic acids. There is also formed in large quantity a crystalline compound, not noticed by Mulder, which Liebig, who discovered it, calls Tyrosine; and, lastly, Leucine, which, according to the above equation, should form 30 per cent. of the products derived from the substance (albumen, &c.) decomposed, does not, in fact, occur in a much larger proportion than 2 per cent. It is obvious, therefore, that the study of the products of decomposition of the albuminous compounds is in a very imperfect state, and must be prosecuted diligently before we can expect trustworthy results. This important investigation is at present occupying the attention of several eminent chemists, and we may hope, ere long, to be enabled to fix, in this manner, the formulæ of the substances now under consideration.

In the meantime, having given the above brief sketch of the state of our knowledge on this subject, and of the views of Mulder, which

have hitherto been generally adopted, we shall not attempt to give formulæ for the albuminous compounds, but describe them according to the latest authorities.

Albumen.—This important substance forms the white of eggs, and occurs in large quantity in the blood. It is also found in other animal fluids, and in most of the animal solids.

It occurs also in many vegetable juices, and in many seeds, such as nuts, almonds, &c. From whatever source it is obtained, its properties are the same.

Albumen is naturally soluble in water, and is found dissolved in the serum of the blood, and in vegetable juices. The white of eggs is quite soluble; and the albumen of wheat-flour also dissolves in water, if it have been purified without the application of heat. But, when it has once been heated to 160° , it becomes insoluble; and, if previously dissolved, a heat of 158° causes the dissolved albumen to coagulate, and the coagulum is insoluble in water. Hence albumen is described in two states, the soluble and the coagulated.

If white of egg, or serum of blood, be dried up at 120° , the residue is soluble albumen in an impure state. It is purified by being well washed with cold ether and alcohol, which remove fat, salts, and other foreign matters.

Dry soluble albumen, when placed in water, first swells up, and then forms a glairy fluid. This solution is coagulated by heat, by acids, by alcohol, by creosote, &c. The acids which do not coagulate albumen are acetic acid, phosphoric and pyrophosphoric acid. The coagulated albumen dissolves with the aid of heat in strong hydrochloric acid, producing a purple solution. This reaction applies to all albuminous compounds, or, as they are often called, the modifications of proteine, and indicates a great similarity of constitution among them.

The solution of albumen is also coagulated or precipitated by the ferrocyanide of potassium if acetic acid be added, by the acetate of lead, and the bichloride of mercury; also by infusion of galls. From the insolubility of the precipitate with bichloride of mercury, white of egg, beat up with water, is used as an antidote to that poison. One egg combines with about four grains of corrosive sublimate.

The precipitates formed by acids are compounds of albumen with the acid employed. They are soluble in pure water, but quite insoluble in diluted acids.

Coagulated albumen is quite insoluble in water, but is readily dissolved by caustic alkalies, which it even neutralizes. These compounds yield insoluble albuminates with the metallic salts.

Coagulated albumen, when acted on by hydrochloric acid, yields

from 1 to 2 per cent. of phosphate of lime; and soluble albumen appears to possess the property of dissolving that salt, a property which perhaps enables the blood to convey to the bones their earthy part, and probably also to carry to the kidneys that which is found in the urine.

The composition of albumen has been ascertained by a number of experimenters, but we have not yet obtained data sufficient to fix its empirical formula, while its atomic weight and rational formula are quite unknown. It is true that Mulder has endeavoured to prove that blood-albumen is composed of 10 eq. of proteine, 2 eq. of sulphur, and $\frac{1}{2}$ eq. of phosphorus; and that egg-albumen contains only 1 eq. of sulphur. But we have already explained that the existence of proteine, as defined by him, is extremely doubtful; and, even if we were to admit its existence, it would appear that Mulder himself now regards proteine as a complex substance. Further, the presence of unoxidized phosphorus has not been established by any sufficient evidence; and egg-albumen really contains more sulphur than blood-albumen. It is safer, therefore, and less likely to mislead the learner, not to assume the presence of proteine, and to give simply the most recent analyses of albumen, which also indicate more sulphur than corresponds to Mulder's formula.

The analyses of albumen by Mulder, corrected according to the now admitted atomic weights ($H=1$; $C=6$; $N=14$; $S=16$), give the following results:—

	Albumen of Eggs.	Albumen of Blood.
Carbon	53.731	54.086
Hydrogen	7.020	7.100
Nitrogen	15.520	15.650
Oxygen	22.921	22.157
Phosphorus	00.430	00.330
Sulphur	00.378	00.677
	100.000	100.000

These analyses are not sufficiently in accordance with those since made by other chemists, to allow us to deduce any formulæ from them.

Scheerer obtained the following results:—

	Albumen of Eggs.	Albumen of Blood.	
Carbon	55.000	55.461	55.097
Hydrogen	7.073	7.201	6.880
Nitrogen	15.920	15.673	15.681
Oxygen	} 22.007	21.665	22.342
Sulphur			
Phosphorus			
	100.000	100.000	100.000

One source of difficulty in these analyses is the presence of inorganic matter, such as phosphates, which does not, perhaps, exist in the albumen in the same form as that in which it is found in the ashes. The

quantity of ash appears somewhat variable. Scheerer found rather more than 2 per cent. Mulder found about the same quantity, but apparently did not make the proper allowance; and, in the subjoined analyses by Weidenbusch of the albumen contained in the juice of the flesh of fowl and fish (pike), the ash did not exceed 0·2 per cent.

	Albumen from Flesh of Fowl.		Albumen from Flesh of Pike.	
Carbon . . .	53·05	53·31	52·64	52·50
Hydrogen . . .	7·10	6·96	7·31	7·26
Nitrogen . . .	15·82	15·69	16·48	16·65
Sulphur . . .	1·55	1·57	1·61	1·57
Oxygen . . .	22·29	22·28	21·76	21·82
Ashes . . .	0·20	0·20	0·19	0·19
	100·00	100·00	100·00	100·00

It will be seen that in these last analyses, made with the aid of the most recent and improved methods, the amount of sulphur is from 3 to 5 times greater than in those of Mulder. This point is of great importance, since, if established, it demonstrates that Mulder's formula must be erroneous; that is, if proteine be, as he maintains, a compound devoid of sulphur. The analyses of albumen by Rüling gave the following results:—

	Albumen of Eggs.				
	I.	II.	III.	IV.	V.
Carbon . . .	51·91	51·88	53·40		
Hydrogen . . .	7·15	7·13	7·01		
Sulphur . . .	1·717	1·703	1·724	1·766	1·796

	Albumen of mixed Venous and Arterial Blood.			
	I.	II.	III.	IV.
Carbon . . .	50·81	53·11		
Hydrogen . . .	7·09	7·01		
Sulphur . . .	1·383	1·384	1·387	1·391

	Albumen of Arterial Blood.		Albumen of Venous Blood.	
	I.	II.	III.	IV.
Carbon . . .	52·74		52·76	
Hydrogen . . .	7·14		7·28	
Sulphur . . .	1·31	1·296	1·283	1·287

It is to be noted here that egg-albumen, which contains, according to Mulder, one-half less sulphur than blood-albumen, and, consequently, had a different formula, appears really to contain more sulphur.

Verdeil obtained, in two very careful analyses,—

	I.	II.
Sulphur in 100 parts of Albumen of Eggs . . .	2·164	2·054

Lastly, recent experiments lead to the conclusion that the amount of nitrogen in albumen has also been under-estimated, and that it probably amounts to 16 or 17 per cent.

When we consider that Mulder's formula for albumen amounts to $C_{400}H_{310}N_{50}O_{120} + S_2 + \frac{1}{2}P$, it is obvious that such variations as the

analyses above given exhibit in all the elements must effectually prevent us from deducing with certainty any such formula. Even the analyses of Mulder himself, when compared with his formula, give results differing from it in *plus* or in *minus* by from 20 to 30 atoms of carbon and of hydrogen, 6 atoms of nitrogen, and 4 atoms of oxygen; and if we compare his results with those of others, especially in regard to the carbon, the nitrogen, and, above all, the sulphur, the variations become so great as to prove that our knowledge is not yet sufficiently advanced to enable us to fix the formula of such a compound.

At present, the method which promises best in reference to the fixing the formula of albumen and its congeners, is that of studying minutely the products of their decomposition when they are acted on by powerful reagents, such as caustic potash, aided by heat, hydrochloric acid, sulphuric acid and bichromate of potash, and other means of oxidation.

Licbig has lately shewn that caseine when heated with potash gives rise to two crystallized compounds, one of which is *leucine*; the other is a new body, *tyrosine*, both in considerable quantity: and that valerianic acid is also formed, probably by the action of potash on the leucine. Butyric acid also appears in this reaction. Bopp has found that caseine, acted on by hydrochloric acid, yields tyrosine and leucine; and Schlieper and others have found, among the products of oxidation of gelatine and other animal substances, a number of definite products, such as hyduret of benzoyle, butyric acid, aldehyde, butyric aldehyde, valerianic acid, and two new bodies, valeronitrile and valeracetonitrile. These discoveries justify the conclusion that the albuminous substances will be found to be complex but definite compounds, capable of being resolved into less complex constituents, the ascertaining of which will enable us to determine their formulæ in the same way as that of salicine has been fixed by the beautiful researches of Piria. But until that shall be done, it is not at all probable that these formulæ can be ascertained by mere ultimate analysis, however carefully performed.

We have thought it right to enter into some detail in regard to the composition and formula of albumen, as being the type of albuminous compounds. The same considerations apply to fibrine and caseine in every point, and, therefore, we shall not again, under those substances, give the analyses so minutely. But the reader will bear in mind that the formulæ of these bodies are as little ascertained as that of albumen, and that we must look to the same methods for the means of one day fixing these important formulæ.

To prove the presence of unoxidized sulphur in albumen, dissolve it in potash, then add acetate of lead as long as the precipitate formed is

redissolved, and heat the solution to the boiling point. It instantly becomes black by the separation of sulphuret of lead. The same test applies to fibrine and caseine. (Liebig.) It is not known in what state the phosphorus, if any, exists in albumen, after the phosphate of lime has been separated. The foetid smell of putrefying albumen indicates distinctly the presence of sulphuretted hydrogen among the products of its putrefaction.

When the juice of many vegetables, after having been separated from the coagulum or deposit which spontaneously forms in it, and which is vegetable fibrine, is heated, a new coagulum is formed, which is vegetable albumen. When nuts, almonds, and similar seeds are freed from their oil by pressure, the residue is chiefly vegetable albumen in the soluble form. It is in every respect identical with the albumen of eggs and of blood.

Albumen must be considered as the true starting-point of all the animal tissues. This appears from the phenomena of incubation, where all the tissues are derived from the albumen of the white and of the yolk, which contains albumen also, with the aid only of the air, of the oily matter of the yolk, and of a certain proportion of iron, also found in the yolk. It is clear from this, that albumen may pass into fibrine, caseine, membranes, horn, hair, feathers, &c.

It was formerly supposed that the albuminous compounds found in the vegetable kingdom were quite distinct from those in the animal organism; but the researches of Mulder and of Liebig have proved that animal and vegetable albumen, animal and vegetable fibrine, and animal and vegetable caseine, are respectively identical in every essential point.

It appears, also, from the researches of Liebig, that the albuminous compounds are formed by vegetables alone, and that the animal body possesses only the power of converting the one into the other. On this view, animals are entirely dependant on vegetables for a supply of the substances out of which first blood, and then from that fluid all the solids of the body, are produced. For this reason the food of animals must contain albuminous compounds ready formed. Since it is these alone which can contribute to the growth of the body, or the supply of the daily waste, and since they are all derived, directly or indirectly, from plants, the chief object of agriculture is to produce these compounds, and to increase the proportion of them in vegetable products, so as to increase the nutritive power of food, without adding to its bulk. The cultivated varieties of grain, and other esculent vegetables, contain a much larger proportion of albuminous or strictly nutritive matter than the same plants do in the wild state; and, in general, the

nutritive value of any food is proportional to the amount of albuminous matter it contains, other things being the same. We shall see hereafter that food ought also to contain matter adapted to support the function of respiration; and that the best and most truly nutritious food is that which contains the two elements, the strictly nutritive or nitrogenized, and the respiratory or non-nitrogenized, in a certain proportion.

Fibrine.—This substance occurs, like albumen, in two forms, dissolved and coagulated. The former is found in fresh-drawn blood and in fresh-drawn vegetable juices, from both of which it coagulates spontaneously on standing. In the coagulated state it is found in muscular fibre, and in the gluten of wheat-flour and the seeds of the cerealia generally.

The characters of insoluble or coagulated fibrine closely resemble those of coagulated albumen. With strong acetic acid it forms a jelly, which may be dissolved by boiling water, and is precipitated by ferrocyanide of potassium. It is similarly acted on by other acids; and, like albumen, dissolves in alkalies, which it neutralizes. It gives a purple solution with strong hydrochloric acid.

When fresh blood is allowed to stand, the fibrine dissolved in it coagulates very soon, and forms the clot, which, however, is coloured by the globules of the blood; but, if the blood be stirred with a stick while coagulating, the fibrine adheres to the stick in grey stringy masses, which dry, like albumen, into a horny matter. Like albumen, it contains sulphur, and phosphorus (?), and its ashes contain phosphate of lime. It contains rather less sulphur, however, than albumen.

As albumen, during incubation, passes into fibrine, so fibrine in the animal body passes into albumen; for example, in the case of an animal fed on muscular fibre, whose blood contains the usual proportion of albumen. Nay, Denis has shewn that the fibrine of venous blood, by digestion with a solution of nitre, is dissolved, and acquires the characters of albumen, being coagulated by heat and by acids. Scheerer has shewn that the fibrine of arterial blood does not undergo this change, nor that of the buffy coat, nor even venous fibrine after exposure to the air for some time. Hence he concludes that it is rendered incapable of dissolving by the action of oxygen, and that the fibrine of venous and of arterial blood are thus distinct; the former being soluble, the latter coagulated.

He found that the above-mentioned solution of venous fibrine in nitre, when exposed to the air, deposited an insoluble matter, identical with arterial fibrine. He also observed, that, after being boiled for

a short time, venous fibrine became insoluble, and had lost the property, possessed by it when fresh, of absorbing oxygen and giving off carbonic acid.

The fibrine which spontaneously coagulates from certain vegetable juices, such as those of carrots, turnips, and beet-root, and that contained in the gluten of wheat-flour, are identical in properties and composition with animal fibrine.

Fibrine, both animal and vegetable, is a most important element of nutrition; and yields, in the animal body, albumen, caseine, and the tissues derived from them.

Composition of Fibrine.—The analysis of fibrine by different chemists has given the following results:—

	Mulder.	Scheerer.		Rüling.		Verdeil.	
Carbon .	53·810	54·454	55·002	52·08	52·18	..	
Hydrogen .	6·910	7·069	7·216	7·09	7·06	..	
Nitrogen .	15·539	15·762	15·817	..	..	..	
Oxygen	23·052	22·715	21·965	..	..	..	
Phosphorus	0·330			S 1·368	1·270	1·587	1·6
Sulphur	0·359			..	..		

In the following analysis the nitrogen amounted to a larger percentage than above exhibited:—

	Melsens.	Unger and Strecker.		Dumas and Cahours.
Nitrogen in 100 parts of Fibrine	19·5	17·21	17·33	16·0

The above numbers prove that we are not in a condition to determine the formula of fibrine, which will be more probably ascertained from the products of its decomposition, as explained under albumen.

Caseine.—This, the third important albuminous body, is found in milk, and constitutes that ingredient which is neither coagulated spontaneously, like fibrine; nor by heat, like albumen; but by the action of acids alone. Cheese, made from skimmed milk and well pressed, is nearly pure caseine. A substance quite identical is found abundantly in the seeds of leguminous plants, and was formerly called *Legumine*. Liebig has recently shewn that legumine is nothing but caseine; and, from whatever source, it is found to have the same properties. Thus its analysis gives nearly the same results as those of fibrine and albumen for the four organic elements; and it differs, according to Mulder, from these bodies in containing no free phosphorus. Its ashes are very rich in phosphate of lime and in potash; and in this point also animal and vegetable caseine agree.

Coagulated caseine is generally a compound of caseine with the acid

employed to coagulate it. When milk, on*standing long, coagulates, it is found to contain free lactic acid, some of which by combining with the caseine has caused the precipitate. When sulphuric acid is used, the coagulum is sulphate of caseine; which, when the acid is removed by carbonate of lead, yields pure caseine.

When dry, caseine thus prepared is like gum. It is not readily dissolved by water, and never forms a clear solution. It is precipitated by acetic acid, but in other respects resembles a solution of albumen, except that it is not coagulated by heat. When milk is placed in contact with *rennet*, which is an infusion of the lining membrane of a calf's stomach, it is coagulated. Liebig has shewn, that, unless the membrane be in a state of decomposition, this change does not take place; and it probably depends on the formation, under the fermenting influence of the membrane, of sufficient lactic acid, derived from the sugar of milk, to neutralize the alkali of the milk and thus coagulate the caseine. When sweet milk or cream is used, the cheese contains much butter besides the caseine.

When milk is heated in an open vessel, a pellicle is formed, which, if removed, is continually renewed, and is insoluble. It is owing to the action of oxygen, for it does not form in an atmosphere of carbonic acid. (Scheerer.)

When peas, beans, or lentils are softened in cold water, then ground with that fluid, and the mass further diluted, and strained through a fine sieve, there passes through a solution of caseine in which starch is suspended. When the starch has settled, the supernatant liquid is a solution of caseine, which is always, like milk, turbid, partly from suspended fat, partly from the gradual action of the air on the dissolved caseine, (*qu.* on sugar?), lactic acid being slowly formed, which causes a gradual separation.

This solution has all the characters of skimmed milk; it is coagulated by acids, not by heat, and forms a pellicle when heated. It also coagulates after long standing from the formation of lactic acid; and, when the coagulum putrefies, the odour is exactly that of putrid cheese. (Liebig.)

The ashes of soluble caseine, whether animal or vegetable, are very strongly alkaline; and there is reason to believe that the potash found in the ashes had served, by combining with the caseine, to render it soluble.

Caseine occurs also in the oily seeds, such as almonds, nuts, &c., along with albumen, and must be considered as a very important element of nutrition.

Scheerer, by acting on the serum of blood with water and a little

caustic potash, obtained a neutral solution, which no longer coagulated by heat, but formed a pellicle like milk. As this pellicle appeared identical with that from milk, the experiment seems to prove the conversion of albumen into caseine.

Mulder considers caseine to be $10Pr + S$; but pure caseine is not known, and caseine, as it usually occurs, contains 6·5 per cent. of inorganic matter, chiefly phosphate of lime and potash. There is no doubt, however, that the organic elements of caseine are united in nearly the same proportions as those of albumen and fibrine; while, like the two latter, it yields a purple solution when heated with strong hydrochloric acid. The action of milk, also, in the nutrition of young animals proves that caseine is capable of conversion into albumen and fibrine; while the production of milk in an animal fed on albumen or fibrine, or both, shews that these bodies may be reconverted into caseine.

The formula of caseine must be regarded as unknown; for, as in the case of albumen and fibrine, the analyses give discordant results, and even the best analyses do not suffice to determine the formula, as long as the atomic weight is unascertained. The analyses of the caseine of milk have yielded the following results:—

	Mulder.	Scheerer.			Rüling.		
Carbon	52·207	54·825	54·665	54·580	53·43	53·26	53·71
Hydrogen	7·160	7·153	7·465	7·352	7·15	7·08	7·09
Nitrogen	15·618	15·628	15·724	15·696	..	..	..
Oxygen	22·656	22·394	22·146	22·372	S 1·015	0·85	1·017
Sulphur	0·359						
	100·000	100·000	100·000	100·000			

According to Walther, the amount of sulphur in caseine, in three analyses, was 0·996, 0·857, and 0·945 per cent. Verdeil obtained, in two analyses, 0·814 and 0·872 per cent. of sulphur. The average of all is 0·92 per cent. of sulphur; decidedly less, therefore, than is found in albumen and fibrine.

The legumine of almonds, a substance closely analogous to vegetable caseine, has been found to contain nearly 18 per cent. of nitrogen; but the vegetable caseine of peas and beans has the same composition as that of milk above given.

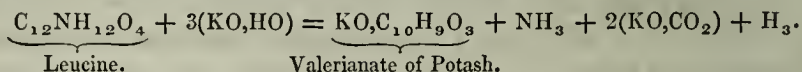
Products of the Decomposition of Caseine.—Schlossberger has observed that the caseine of milk, precipitated by hydrochloric acid, and well washed, dissolves in water by digestion at a gentle heat, and that the addition of a little carbonate of ammonia to the solution causes a precipitate of a cascous substance, having apparently the composition

and characters of an albuminous or proteine compound, and containing sulphur. The liquid filtered from this body yielded, on the addition of hydrochloric acid, a second precipitate containing no sulphur, and apparently less nitrogen than the albuminous or proteine compounds usually do. These observations render it probable that caseine is formed of at least two albuminous bodies, one of which contains no sulphur.

Tyrosine.—Liebig has discovered that when pure cheese is melted with caustic potash till hydrogen begins to come off along with the ammonia which is at first disengaged, the residue, dissolved in hot water and mixed with a slight excess of acetic acid, deposits on cooling a mass of fine needles, which are sparingly soluble in cold water, and insoluble in alcohol and ether. These crystals are a new compound, which Liebig calls *tyrosine*, and the empirical formula, deduced from his analysis, is $C_{16}NH_9O_5$. It is soluble in alkalis, but combines with acids. This remarkable compound merits a detailed investigation. Its composition and power of combining with acids would seem to indicate that it is a basic compound.

Leucine.—The mother-liquid which has deposited tyrosine, when still further concentrated, yields a large quantity of *leucine*, a crystallized substance, formerly known as a product of the action of potash on gelatine and the albuminous compounds. The formula of leucine is $C_{12}NH_{12}O_4$. It forms white scales, volatile at 338° . With nitric acid it forms a compound acid, *nitroleucic acid*, not fully studied.

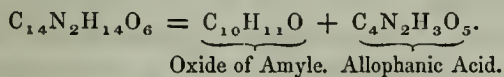
When the mass obtained by melting caseine with potash is supersaturated with tartaric acid and distilled, it yields *valerianic acid*; and when the fusion has been longer continued, *butyric acid* is also obtained. Liebig has shewn that leucine, when heated alone with potash, yields ammonia (and hydrogen?), while valerianate of potash (along with carbonate?) is left. This is easily explained:—



It would appear from this that leucine is first formed, and that the valerianic acid is formed by the decomposition of leucine by potash.

Leucine contains, with the exception of 1 atom of hydrogen which is wanting, the elements of a compound of 1 eq. of cyanic acid, 1 eq. of oxide of amyle, and 2 eq. of water. But when hydrated cyanic acid is made to act on hydrated oxide of amyle, the crystalline compound produced, although in appearance exactly similar to leucine, is really a different substance, being soluble in ether, in which leucine is insoluble. This last compound is the allophanate of oxide of amyle,

perfectly analogous to the allophanates of the oxides of ethyle and methyle, discovered by Liebig and Wöhler. Its formula is—



According to Bopp, the details of whose experiments have not yet been published, caseine, when heated with hydrochloric acid, yields several products, the chief of which are tyrosine and leucine. It was long ago observed by Mulder that albuminous or proteine compounds yield leucine when acted on by sulphuric acid. It would seem, therefore, that the albuminous bodies are capable of being resolved into crystallizable and definite compounds, the study of which presents the only feasible method of determining their formulæ.

It has further been found, although the details are not yet published, that caseine, when oxidized by certain methods, yields the same series of products as gelatine, namely, hyduret of benzoyle, butyric acid, aldehyde, butyric aldehyde, valerianic acid, valeronitrile, and valeracetoneitrile. These facts, if confirmed, justify us in expecting that the true constitution and formulæ of caseine and the other albuminous bodies will be ere long satisfactorily ascertained.

The spontaneous decomposition of caseine confirms these views, for putrid cheese is found to contain valerianic, butyric, caproic, caprylic, and capric acids, derived no doubt from some of the products, such as leucine, into which caseine may be resolved. The same remark applies to the putrefaction of fibrine, which yields butyric acid.

It has already been mentioned, that cheese, in a certain state of decomposition, possesses the remarkable property of causing sugar to undergo the lactic fermentation, and that, if the contact of the decaying or putrefying cheese be continued at a slightly higher temperature, the lactate of lime (formed by the action of the lactic acid as it is formed on chalk added to the mixture) is made to undergo the butyric fermentation, and entirely converted into butyrate of lime, hydrogen being disengaged. It would be desirable to ascertain how far the power of inducing the butyric fermentation may be owing to the presence of butyric acid in the putrefying cheese.

Gelatinous Tissue.—Under this name are included the organic tissue of the bones, that of tendons and ligaments, the cellular tissue, the skin, and the serous membranes. All these substances dissolve by long-continued boiling in water, and the solution on cooling forms a jelly. The coarser forms of gelatine, from hoofs, hides, &c., are called *Glue*; that from skin and finer membranes is known as *Size*; and the purest gelatine, from the air-bladders and other membranes of fish, is

called *Isinglass*. Gelatine does not exist as such in the animal tissues, but is formed by the action of boiling water.

Gelatine is soluble in water, and the hot concentrated solution forms a jelly on cooling. It is precipitated by tannic acid, forming an insoluble compound, which forms the chief part of leather. Leather is made by steeping softened skins in a strong infusion of oak-bark, catechu, or other astringent vegetables containing tannic acid. Skins are prepared in other ways, yielding different kinds of leather, such as tawed leather, wash-leather, &c.; but the process of tanning depends on the action of tannic acid on the gelatinous tissue.

Gelatine, when acted on by sulphuric acid, yields *gelatine sugar* or *glycocoll*, $C_4NH_4O_3.HO$. When treated with potash, it is said to yield glycocoll and leucine.

According to Scheerer, the composition of gelatinous tissue is represented by the formula $C_{48}H_{41}N_{7\frac{1}{2}}O_{18}$, or doubled, $C_{96}H_{82}N_{15}O_{36}$; which latter formula represents, on the proteine theory, 2 at. proteine + $3NH_3 + HO + O_7$.

Although gelatine is thus nearly related to the albuminous bodies, and is doubtless formed from one or other of them, yet it has none of the characters of these compounds. It does not yield proteine when acted on by potash, and it does not produce a purple colour with hydrochloric acid. It is evidently, therefore, in some respects distinct from them. It has lately, however, been shewn that gelatine contains sulphur, and is more closely allied to the ordinary albuminous compounds than was formerly supposed. The amount of sulphur in isinglass is from 0.56 to 0.727 per cent., twice as much as was formerly found in albumen by Mulder. It would appear, however, that gelatine cannot, in the animal body, be transformed into albumen, fibrine, and caseine. This explains the fact, that animals fed exclusively on gelatine die with the symptoms of starvation.

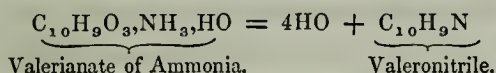
Blood cannot be made from gelatine, and the animal, therefore, soon dies. But when mixed with other food, especially albuminous compounds, gelatine may be useful, and may serve directly to nourish the gelatinous tissues. (Liebig, *Animal Chemistry*, 98, 130.) This would explain the use of gelatine as a part of the food of convalescents, whose debilitated system cannot readily convert albumen, &c. into gelatine for the nutrition of these tissues, and finds it ready-made in the food. The experiments of D'Arcet on the gelatine from bones have proved, that, as part of the diet in hospitals, gelatine produces the best effects, and materially abridges the period of convalescence. When it is given alone, all animals soon refuse it with disgust, and die if confined to gelatinous food.

The analysis of gelatine has given the following results:—

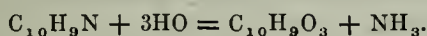
	Scheerer.		Schlieper.		
Carbon	50.557	50.774	50.50	∴	∴
Hydrogen	6.903	7.188	6.90	∴	∴
Nitrogen	18.790	18.320	18.47	∴	∴
Sulphur }	23.750	23.532	{ S 0.56	0.468	0.505
Oxygen }			{ O 23.57	∴	∴
	100.000	100.000	100.000		

Products of Decomposition of Gelatine.—Schlieper has recently examined the products of the oxidation of gelatine by means of bichromate of potash and sulphuric acid. Among these products he discovered, 1. hydrocyanic acid; 2. acetic acid; 3. valerianic acid; 4. benzoic acid; 5. a new oil, *valeronitrile*; 6. another new oil, *valeracetonitrile*; and, 7. a heavy oil, with an odour of cinnamon, not fully studied.

Valeronitrile ($C_{10}H_9N$) is precisely analogous to benzonitrile, and is derived from valerianate of ammonia as follows:—

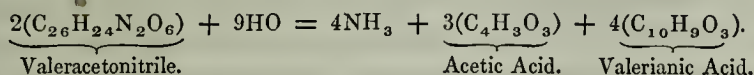


When acted on by alkalies, valeronitrile, taking up 3 eq. of water, is resolved into valerianic acid and ammonia:—



The ammonia escapes, and the acid is retained by the alkali. Valeronitrile is a fluid, highly refracting, colourless oil, of sp. gr. 0.81, with a burning aromatic taste, and a smell like that of oil of bitter almonds mixed with that of hyduret of salicyl.

Valeracetonitrile resembles valeronitrile, but is more volatile, and has the sp. gr. 0.79. Its formula is $C_{26}H_{24}N_2O_6$, which contains the elements, if 2 eq. be taken, of 4 eq. valeronitrile, and 3 eq. hydrated acetic acid. It is resolved by alkalies, water being taken up, into ammonia, which is given off, and acetic and valerianic acids, which combine with the alkali.



According to Marchand, oil of bitter almonds, or rather hyduret of benzoyl, is also formed in the oxidation of gelatine. The occurrence of benzoic acid renders this probable, although Schlieper could not obtain the oil.

It is evident that the prosecution of these researches will enable us to determine the formula and constitution of gelatine, which, however, we must consider, for the present, as unknown.

Chondrine.—This substance forms the tissue of cartilage as it occurs in the ribs, trachea, nose, &c., and of the cornea. It is slowly dissolved by boiling with water, and when dry resembles glue. But it differs from gelatine in not being precipitated by tannic acid, and in giving precipitates with acetic acid, alum, green vitriol, and acetate of lead. Bones, when in the cartilaginous state, are composed of it. According to Scheerer, it is composed of $C_{48}H_{40}N_6O_{20}$; that is, on the theory of proteine, of $\text{proteine} + 4HO + O_2$. Chondrine leaves, when burned, from 4 to 6 per cent. of ashes, chiefly bone-earth.

Arterial Membrane.—The middle coat of the artery, which is a very elastic membrane, leaves, when burned, 1.7 per cent. of ashes. According to Scheerer, it is composed of $C_{48}H_{38}N_6O_{16}$; that is, $\text{proteine} + 2HO$.

Horny Matter.—This occurs in two forms, *membranous* and *compact*. The former constitutes the epidermis, and the epithelium or the lining membrane of the vessels, of the intestines, and of the pulmonary cells. The latter forms hair, horn, nails, &c.

Scheerer has analyzed numerous specimens of both kinds of horny matter, and deduces from his results the formula $C_{48}H_{39}N_7O_{17}$; that is, $\text{proteine} + NH_3 + O_3$.

Horny matter, when acted on by potash, yields proteine on the addition of acetic acid.

Feathers are closely allied to horny matters, but, according to Scheerer, contain 1 at. of oxygen less; the formula of feathers, deduced from his analysis, being $C_{48}H_{39}N_7O_{16}$.

Pigmentum nigrum Oculi.—This substance, according to Scherer, contains more carbon than any of the preceding; but its formula has not been ascertained.

It is to be particularly observed, that the formulæ above given for the principal tissues of the body are only intended to shew generally the relation they actually bear to the albuminous or proteine compounds. It is not meant that they are formed in the body by the addition of water, ammonia, or oxygen to proteine: on the contrary, we are as yet ignorant of the conditions under which they are produced; and in some cases, as for example in gelatine, several different views may be taken of their formation; while the existence of proteine, as we have explained, is entirely problematical.

THE BLOOD.

This important fluid, from which all parts of the body are formed, possesses very remarkable properties. In the veins it is dark-coloured,

in the arterics bright red. When drawn, it presently forms a red clot, composed, as we have seen, partly of fibrine, while the serum contains a large quantity of albumen.

The colour of the clot is owing to a compound which has been called *Hæmatosine*, which has many properties in common with albumen; but the globules of the blood, in which the colour naturally resides, are not composed of hæmatosine alone, but contain another albuminous compound, to which the name of *Globuline* has been given. It is probable that neither of these compounds is known in a state of purity.

To obtain them, blood is well stirred to separate the fibrine, and mixed with 6 volumes of a saturated solution of sulphate of soda, in which the globules are insoluble. They are then boiled with alcohol acidulated with sulphuric acid, which dissolves a sulphate of hæmatosine, and leaves a sulphate of globuline. The red alcoholic solution is mixed with carbonate of ammonia, which separates the sulphuric acid as sulphate of ammonia, along with a little globuline. The filtered solution, being evaporated, leaves hæmatosine as a dark brownish-red mass.

Hæmatosine thus prepared is insoluble in water, alcohol, and ether, but forms red solutions with alcohol, to which either acids or alkalies are added. Its ashes contain iron, but Liebig and Scheerer have shewn that the red colour does not depend on that metal, which may be removed either from the globules or from hæmatosine by strong sulphuric acid, without destroying the red colour; and in this experiment the red matter left gives a white ash, free from iron. Iron, however, is essential to the blood, and is consequently supplied in the food. The ashes of almost all vegetables contain a little iron; flesh of course does so, as it is mixed with blood; and the yolk of egg is found to contain an oily matter, of which iron is an ingredient.

Globuline forms the principal part of the blood-globules. It has not been obtained in a pure state, but has all the characters, as well as the composition, of dissolved albumen. The compound with sulphuric acid above mentioned is grey, or white, and was found to contain 4 atoms of sulphuric acid and 1 of proteine.

Besides albumen, the serum of the blood contains fat and saline matters. When heated, the albumen coagulates, and floats in a watery liquid called the *Serosity*. This contains common salt, sulphates, and phosphates. The serum, and consequently the blood, is always alkaline from phosphate of soda, but no carbonate is present. The blood also contains the ingredients of the secretions and excretions, such as bile and urine; but these are in so small a proportion, that, except

in cases of disease, it is hardly possible to detect them. The fatty matter in blood is obtained by drying up the serum and digesting with ether. It consists of the usual animal fats, and is said likewise to contain cholesterine, or the fat of bile.

The following table gives the results of two careful analyses of blood by Lecanu :—

Human Blood.		
Water	780·145	785·590
Fibrine	2·100	3·565
Colouring Matter (Hæmatosine and Globuline) . .	133·000	119·626
Albumen	65·090	69·415
Crystalline Fat	2·430	4·300
Oily Matter	1·310	2·270
Extractive Matter (soluble in Water and Alcohol) .	1·790	1·920
Albuminate of Soda	1·265	2·010
Alkaline Chlorides, Carbonates, Phosphates, and Sulphates	8·370	7·304
Carbonates of Lime and Magnesia, Phosphates of Lime, } Magnesia, and Iron, Peroxide of Iron . . . }	2·100	1·414
Loss	2·400	2·586
	1000·000	1000·000

It is obvious, that, as the blood is chiefly composed of albuminous compounds, its composition cannot be very different from that of those substances. In fact, dried blood, when analyzed, yields the formula $C_{48}H_{39}N_6O_{15}$, which is proteine, $C_{48}H_{36}N_6O_{14} + HO + H_2$. (Playfair and Boeckmann.) This excess of hydrogen is probably derived from the presence of fat. But these formulæ are to be regarded merely as rude approximations intended to convey a general notion of the composition of blood as compared with that of the so-called proteine compounds.

From the blood, that is, from the albuminous compounds in the blood, are derived all the animal tissues.

Muscular tissue, or *Muscular fibre*, is composed chiefly of fibrine, mixed however in the ordinary state with blood, membranes, nervous matter, and fat. Dried flesh, when analyzed, gave the same formula as dried blood, namely $C_{48}H_{39}N_6O_{15}$. (Playfair and Boeckmann.)

Juice of Flesh.—Besides the blood, and the fluids contained in the lymphatic and absorbent vessels, there exists in flesh a considerable quantity of a peculiar fluid, enclosed either in peculiar minute vessels, or more probably in the cells of the fibrous and cellular tissues. To this liquid Liebig gives the name of the *juice of flesh*, and he has lately subjected it to a minute investigation, with very important results. The details of these researches will be found in his late work, “*Researches on the Chemistry of Food*,”* where the reader will also find many interesting applications to physiology, to medicine, to dietetics, and to the art of cookery.

* London, Taylor and Walton, 1847.

The only observations on the nature of the fluid of flesh previously made were those of Chevreul and of Berzelius, which, however, were chiefly confined to the liquid, or soup, obtained by boiling flesh with water. To the sapid extract of meat thus prepared the name of *osmazome* was given; but this, as now appears, was a very complex mixture. Chevreul also discovered a very remarkable crystalline compound, which he called kreatine (from *κρεας*, flesh); but he did not ascertain its composition, and Berzelius was not able to procure it. Other chemists were equally unsuccessful, and Wöhler only obtained, from beef soup, enough to prove that it was not allantoine; while, still more recently, Schlossberger succeeded in procuring a few grains of it from the flesh of an alligator, and confirmed Chevreul's description of its properties.

It had long been known that the juice of flesh was strongly acid, while blood is always alkaline. It was of great importance to ascertain the nature of the free acid or acids present, as also of the bases combined with them, and also to determine whether kreatine was a constant ingredient, or, as Berzelius supposed, an accidental product of decomposition.

The juice of flesh, according to Liebig, is best examined in the following manner:—The flesh of newly-killed animals, the blood being withdrawn to the utmost, and all visible fat, tendons, vessels, &c. having been separated as completely as possible, is finely chopped and mixed with its own weight of pure cold water, with which it is kneaded. The whole is then strained in a bag of coarse linen, and the last portions of liquid expelled by a powerful press. The solid residue is again treated in the same way, and, if necessary, a third time. All the liquids are then mixed and strained to remove any solid particles. The strained liquor is simply the juice of the flesh considerably diluted. The insoluble residue consists chiefly of fibrine, with the smaller vessels and nerves, as well as the cellular tissue, and amounts when dry to 17 or 18 per cent. of the weight of the flesh. The ordinary kinds of flesh contain from 76 to 79 per cent. of water; it is obvious, therefore, that the matters soluble in cold water do not exceed from 4 to 6 per cent. Now, as these soluble matters consist of a considerable number of compounds, both organic and inorganic, it is necessary to operate on a large amount of flesh in order to be able to study them to advantage. It is not advisable to operate with less than 8 or 10 lb. of flesh, which will yield only from 6 to 8 oz. of soluble matter.

The diluted juice of flesh thus obtained is turbid, and of a reddish tinge, more or less dark, according to the kind of flesh. It is in all

cases strongly acid, and has a strong taste and smell of meat. It is introduced into a glass globe or matrass, which is placed in a vessel of water; and the water being made to boil, the solution is gradually heated till the albumen coagulates, which takes place under 140° , yielding a coagulum nearly colourless. When the temperature rises to 158° , the colouring matter of blood (some of which is always present in the juice of flesh) separates as a dark brown coagulum. The heat is continued till a filtered portion, when boiled in a tube, remains clear. The whole is then strained and pressed, and the clear liquid, now free from albumen and all coagulable matters, is nearly colourless, and still strongly acid. The albuminous coagulum when dried amounts to from 2 to 3 per cent. of the weight of the flesh.

The acid liquid now contains all the soluble inorganic ingredients, as well as the organic ingredients soluble in cold water and not coagulated by heat, which the flesh originally contained. Among the former are phosphoric acid, potash, chloride of potassium, chloride of sodium, magnesia, and lime. Among the latter are lactic acid, a new acid called isosinic acid, and one or two other acids, kreatine, kreatinine, (a base formerly described), and some soluble albuminous compounds.

It is found, that, if the liquid be concentrated by evaporation, even at a low temperature, such as 110° or 120° , while the free acid is left to act on the other substances, it acquires, when brought to a syrupy consistence, a dark brown colour, and generally deposits no crystals of kreatine on standing. Occasionally, however, it deposits a very small quantity, as in Chevreul's first experiment, and in that of Schlossberger with the alligator's flesh above mentioned. Having thus ascertained the cause of the difficulty in obtaining kreatine, Liebig was enabled to suggest a method of obviating the usual result. It is only necessary to neutralize the free acid by adding baryta-water as long as it produces a white precipitate. The liquid becomes distinctly alkaline to reddened litmus paper before this point is reached; but Gregory observes, that, when turmeric paper is rendered distinctly brown, the proper quantity of baryta has been added. The white precipitate is phosphate of baryta, and contains the whole of the phosphoric acid in the juice. Its quantity is very considerable; and, as it in almost every case dissolves without residue in hydrochloric acid, it is obvious that the juice contains no sulphuric acid or sulphates. When a trace of sulphuric acid is found, it is derived from the mixture of a little blood with the juice.

The phosphate of baryta is next separated by filtration, and the filtered liquid, which is quite limpid, almost colourless, and very slightly alkaline, is now evaporated in the water-bath at a moderate heat, not

exceeding from 130° to 140° , in large shallow dishes. During the concentration a little insoluble matter separates, which is chiefly carbonate of baryta, formed by the action of the air on the slight excess of baryta. When the whole is reduced to a moderate bulk it is again filtered, and the clear liquid further concentrated at the same heat (130°) in the water-bath to the consistence of a thin syrup. In the case of beef, a mucilaginous skin forms on the surface towards the end of the evaporation, which must be removed. In the case of veal and horse-flesh a number of such skins are formed in succession, and must be removed as often as they form. The precise nature of the matter of which these films are composed is not yet ascertained. It swells up in water without dissolving, and is probably a modification of albuminous or of gelatinous matter. The liquid is then allowed to stand for a day in a temperature of from 80° to 90° , and finally set aside in a cold place for two days. Crystals generally begin to appear while it is yet warm, and at last form in considerable quantity. These crystals, which are usually rather large and transparent, are composed of kreatine, and are easily purified by dissolving them in 6 or 7 parts of boiling water, which deposits the greater part on cooling in brilliant colourless prisms.

It often happens, especially with the flesh of fowl, of pigeon, of the ox, ox-heart, horse, &c., that after the last filtration, and towards the end of the evaporation, a brown, somewhat flocculent powder separates, and is mixed with the crystals. It can be poured off with the mother-liquid when the crystals are large, but when they are small it must be collected on the filter with them. Gregory has found that this powder, which dries up on the filter to a membranous coherent mass, is chiefly composed of kreatine. In one experiment with ox-heart he obtained no crystals, but only this powder, which, however, was dissolved almost entirely by boiling water, and yielded rather more kreatine in proportion to the flesh employed than was obtained in another similar experiment, in which crystals were obtained at first.

The above process applies to all the kinds of flesh usually met with; to the flesh of fowls, pigeons, oxen, ox-hearts, sheep, horses, pig, calf, roe-deer, red-deer, fox, marten, and hare. In the case of pike, the only fish within reach of Liebig, it was found impossible to use the press, from the gelatinous character of the flesh. Liebig, therefore, mixed it with twice its weight of water, and threw the whole on a canvass filter, or bag, where, after it had drained, the liquid retained by the flesh was displaced by the cautious addition of cold water above. The solution, which had a strong smell and taste of fish, was then treated as that of the other kinds of flesh; and the only peculiarity observed was, that, when evaporated to a thin syrup,

it formed on cooling a thin jelly, in which the crystals of kreatine were deposited on standing.

Gregory states that he has found no difficulty with skate and cod, the only kinds of sea-fish which he has tried. These kinds of fish are even more easily pressed than butcher-meat or fowl; less water is required to extract their soluble ingredients; and they possess also this advantage, that no powder separates along with the crystals. He recommends to evaporate to such a degree that on cooling a very thin jelly is formed, and to let this stand for two days. A sufficient quantity of cold water is then added to liquefy the jelly, which is easily dissolved, and on letting it settle for a few minutes, the crystals fall to the bottom, and are found, when the liquid is poured off, so pure as to be hardly coloured, large and well formed, and so clean, that, on dissolving them in hot water, it is not necessary to filter the solution as in the case of fowl, beef, ox-heart, &c., in which the kreatine is, moreover, not so nearly colourless.

The amount of kreatine in the different kinds of flesh yet examined is very different. In all it is small, varying from 0·607 to 3·21 per 1000.

						Liebig.	Gregory.
1000 parts of the flesh of	Fowl	yielded of Kreatine	.	.	3·20	3·20	{ 3·21 2·90
"	"	Ox-heart	"	"	..	..	{ 1·375 1·418
"	"	Cod	"	"	..	..	{ 0·935 1·710
"	"	Pigeon	"	"	..	..	0·825
"	"	Horse	"	"	0·72	0·72	..
"	"	Ox	"	"	0·697	0·697	..
"	"	Skate	"	"	..	..	0·607

In the case of the pigeon's flesh, Gregory mentions that there seemed to have been a loss in consequence of the heat of the weather, and an accidental delay in the process having caused a certain degree of putrefaction, afterwards arrested. It is remarkable that the solution, when apparently undergoing some kind of putrefaction, acquired a strong odour of stale urine, and yet contained no free ammonia, but was neutral. In this case, also, there was formed, along with the crystals, a large quantity of the powder above mentioned, the greater part of which had been thrown away before it was found to contain kreatine. The small portion left, when boiled with water, did yield kreatine; so that it seems probable that the amount really contained in pigeon's flesh is larger than that in the table which was actually found.

Although fowl contains so much more kreatine than any other kind of flesh yet tried, yet the best and most economical source of kreatine is cod or skate. The flesh of fowl when cleaned costs 4s. per pound,

whereas the cleaned fish costs only 4*d.* or 5*d.* per pound at most. The whole operation is easier, and the kreatine is obtained in a state of nearly perfect purity in the first crystallization from the gelatinizing liquid. When once re-crystallized in water, without filtration or the use of any decolorizing agent, it becomes snow-white and chemically pure. Gregory obtained from 25 lb. of cleaned cod 6 drachms avoirdupois of kreatine, or 164 grains; and in a second experiment, from 30 lb. of cod the unexpectedly large amount of 13 drachms, or 356 grains.

Kreatine.—When pure, this substance forms either light, acicular, brilliant prisms of considerable length, or short, thick, transparent crystals of adamantine lustre and of pretty large size: the latter occur when it is deposited from a less concentrated solution. When heated to 212° they become opaque, losing their water of crystallization, which amounts to 2 eq. = 12.08 per cent. It is very soluble in hot water, dissolving easily in 6 or 7 parts at 212°, but is for the most part deposited on cooling, the cold water retaining in solution rather more than $\frac{1}{30}$ th of the weight of the water. If the solution which has deposited crystals be allowed to stand for some days, the crystals increase in size, and much less is retained in solution; and 1 part of kreatine requires about 75 parts of cold water to dissolve it. The solution has a weak bitterish taste. Kreatine is sparingly soluble in alcohol.

Kreatine has neither acid nor basic properties. Its composition is represented by the formula $C_8N_3H_{11}O_6 = C_8N_3H_9O_4 + 2HO$.

By the action of strong acids kreatine is resolved into a new base, kreatinine, $C_8N_3H_7O_2$, and 4 eq. of water. When boiled with baryta it is resolved into another base, sarcosine, $C_6NH_7O_4$, and urea $C_2N_2H_4O_2$, the urea being further resolved, with the aid of 2 eq. of water, into carbonate of ammonia. For details concerning kreatinine and sarcosine, see the section on Organic Bases.

Nothing is yet known in regard to the function performed in the animal economy by kreatine. It is remarkable that both kreatine and kreatinine have recently been discovered in urine; so that it would appear probable that these substances are rather products of change, destined, at all events in part, to excretion, than active agents in the vital processes. The power which kreatine possesses of giving rise to two powerful bases is important; and the full study of the part played by those bases will contribute to explain the action of the vegetable alkaloids on the system.

Lactic Acid, as an ingredient of the juice of flesh, is a substance of great interest. At a time when the composition and properties of lactic acid were altogether unknown, it was supposed, on very imperfect evidence, to be present in flesh; and Cap and Henry more

recently announced the existence of lactic acid in urine, both free and combined with urea. But Gregory, on repeating their experiments, obtained in every trial only pure urea, without any trace of lactic acid, a result confirmed by Pelouze and other observers. Still more recently, Liebig, by experiments made on a very large scale, with all the latest refinements of analysis, could not detect the slightest trace of lactic acid in urine, a result quite opposed to the statements of several French chemists. It is very remarkable that the same observer who has demonstrated the absence of lactic acid in urine, while its absence in blood was proved by Enderlin, should now be the author of the discovery that lactic acid exists in large quantity in the animal body, (although not in these fluids, blood and urine,) namely, in the juice of flesh. From the mother-liquid of the kreatine, lactic acid, which is present in the form of lactate of potash, is easily obtained by adding sulphuric acid, and then alcohol, which dissolves the lactic acid. After purifying it to a certain extent by means of ether, it is combined with milk of lime, and the lactate of lime purified by recrystallization.

We shall hereafter see that the lactic acid performs an important function in the respiratory process, and there is much reason to conclude that it forms an essential part of the free acid in the gastric juice, and thus contributes to digestion.

Inosinic Acid.—This acid is best obtained from the syrupy liquid which has deposited the kreatine, by adding so much alcohol as to render it milky, when on standing a deposit is formed. This is dissolved in warm, not boiling, water, and chloride of barium added; on cooling, inosinate of baryta is deposited in an impure state. It is purified by simple recrystallization in warm water, and forms, when pure, white silvery scales. It is decomposed by boiling. The preparation of this salt, and consequently of the acid, is somewhat difficult, and indeed it appears to be present in very variable quantity, nay, frequently to be absent. Gregory obtained about 61 grains from 7 lb. of fowl, but did not succeed in procuring it from ox-heart or pigeon's flesh. Liebig also often failed to procure it, and it does not appear to occur in fish.

The composition of the acid is $C_{10}N_2H_6O_{10} + HO$. It exists in the juice of flesh as inosinate of potash.

Liebig observed two other organic acids in the juice of flesh, but, from the want of material, these have been hardly investigated, and their composition is unknown, except that they contain nitrogen.

Inorganic Constituents of the Juice of Flesh.—Of these the most important is phosphate of potash. This salt is remarkable for its tendency to assume the peculiar modification $PO_5 \left\{ \begin{array}{l} KO \\ 2HO \end{array} \right\}$, which is an

acid salt, whereas phosphate of soda, the chief mineral salt of the blood, has a most remarkable tendency to form the modification $\text{PO}_5 \left\{ \begin{smallmatrix} 2\text{NaO} \\ \text{HO} \end{smallmatrix} \right\}$, which is alkaline. Soda is also found in the juice of flesh, but on the average the quantity of potash in that fluid is three times that of the soda, and we know that much, if not all of this soda is derived from the blood accidentally mixed with the true juice of flesh, which can never be obtained free from blood. Magnesia is also present; and in the juice of ox-flesh the proportion of phosphoric acid in combination with magnesia is to that united with the alkalies as 2 to 7. The proportion of lime, when present, is so small that it rarely amounts to one-fourth of the magnesia. The juice of flesh also contains chlorine, in the form of the chlorides of potassium and sodium.

It is quite certain that every one of the ingredients of the juice of flesh, organic or inorganic, has its own special function to perform, even although that function be still unascertained. We shall see hereafter the interesting relations between the inorganic constituents of the blood and those of the juice of flesh, and the bearing of these on the vital processes.

The composition of the juice of flesh is of great importance in reference to the use of flesh as food. We shall see that important applications may be made of the researches of Liebig on this subject both to dietetics and to cookery.

Finally, the reader is reminded that the interesting results of which a brief account has been given constitute merely the first steps in a new career of research, and that the nature even of this fluid, the juice of flesh, is still very far from being fully known. By following out, however, the line of research thus indicated, we may expect soon to obtain many most valuable results, of the utmost practical importance, as well as of the highest scientific interest.

BRAIN AND NERVOUS MATTER.

Nervous matter is distinct from all other animal tissues, and is produced by the animal system exclusively. In composition it is intermediate between fat and the albuminous compounds; containing nitrogen, which is absent in fats, but in far smaller quantity than proteine does; and being, on the other hand, much richer in carbon than proteine or its compounds. It appears likewise to contain phosphorus as an essential ingredient.

From the recent researches of Frémy, confirmed by those of Dr. R. D. Thomson, brain appears to contain a peculiar acid, analogous to the

fatty acids, which he calls Cerebric acid, and which contains nitrogen and phosphorus; this is mixed with an albuminous substance, with an oily acid, the *oleophosphoric acid*, with *cholesterine*, and finally with small quantities of oleine and margarine, and of oleic and margaric acids.

The two acids, peculiar to the brain and nervous matter, occur sometimes free, but generally combined with soda or with phosphate of lime.

Cerebric Acid is extracted by ether from the brain after it has been exposed to the action of boiling alcohol, which coagulates the albumen. The matter deposited on cooling by the ether is a mixture of cerebric acid, generally combined with soda or bone-earth, oleophosphate of soda, and a little albumen.

This mixture is acted on by alcohol, acidulated with sulphuric acid, which precipitates sulphate of lime and soda and albumen. The filtered solution contains cerebric and oleophosphoric acids; cold ether removes the latter, and the former is purified by solution in hot ether and crystallization.

When pure, it is white, crystalline, and pulverizable. In hot water it swells up like starch, but does not dissolve. It contains phosphorus, but no sulphur if purified from albumen: the phosphorus amounts to barely 1 per cent.; and it contains 2·3 per cent. of nitrogen. It has the characters of a fatty acid, but its acid properties are feebly marked.

Oleophosphoric Acid.—This acid has not yet been obtained quite pure. With the alkalis it forms soaps, and its compound with soda appears to exist in the brain. When it is long boiled with water or alcohol, it is resolved into oleine and phosphoric acid. This change is accelerated by acids, but it takes place also spontaneously at the ordinary temperature, only more slowly; and the presence of animal matter in a state of decomposition seems to cause it to be resolved into oleine and phosphoric acid. Thus, when brain has been allowed to undergo partial putrefaction, it no longer yields oleophosphoric acid, but oleine and phosphoric acid. It contains 2 per cent. of phosphorus. The oleine of this acid is identical with that of human fat.

Cholesterine.—This fat, as extracted from the brain, in which it occurs in considerable quantity, has the same composition and properties as the fat of biliary calculi. (Couverbe; Frémy.) Frémy has also succeeded in detecting in the liver traces of the characteristic fat acids of the brain.

The grey portions of the brain appear to be chiefly albuminous; while the white portions consist of an albuminous tissue, similar to the grey, but loaded with the fats above described.

The softening of the brain in diseases of that organ seems to be the result of a kind of putrefaction, and is accompanied by the separation

of the oleine from the phosphoric acid. The oleine itself also is decomposed, yielding free oleic acid.

There can be no doubt that the brain and nervous matter (which is quite similar to brain) are formed in the body from albuminous compounds, either by the separation of some azotized compound or compounds, or by the addition of highly-carbonized non-azotized products, such as fats. But we are still ignorant in what part of the body, or by what organs, nervous matter is prepared. This point is worthy of the most minute investigation. In the meantime, according to Chevreul, the fatty matters, which occur in small proportion in the blood, are similar to those of the brain.

The existence of cerebrie and oleophosphoric acids, as well as of several other compounds described by Couerbe and by Frémy, must be considered in so far problematical, that we are not yet assured that these substances are pure and unmixed, so that their true formulæ are undetermined. We shall not, therefore, burden the memory of the reader with formulæ which cannot be expected to be permanent. It is, however, important to bear in mind, that a large part of the constituents of brain has an elementary composition intermediate between that of the albuminous compounds and that of fat, containing, therefore, more carbon and less nitrogen than the common albuminous compounds, and that the brain appears to be much richer in phosphorus than any other of the soft parts, whether that element be entirely in the form of phosphates, which certainly abound in the brain, or partly as phosphates and partly in some other form of combination in which the phosphorus is not oxidized.

The whole subject is one which requires a renewed and very full investigation, and will certainly yield most valuable and important results. In his "Researches on the Chemistry of Food," (1847, p. 47,) Liebig mentions that he has in vain sought for kreatine in the brain; but that when brain is rubbed into an emulsion with baryta-water, and strained through a fine hair sieve, the emulsion on being boiled yields a coagulum containing all the albumen and fat, and a clear liquid containing two salts formed by the union of baryta with two acids. One of these salts is soluble, the other insoluble, in alcohol; both are soluble in water, and the solutions yield with acids white flocculent precipitates. The study of these products promises to shed much light on the constitution of brain. Dr. R. D. Thomson is at present engaged in a minute and comprehensive investigation of the brain, the results of which cannot fail to be both interesting and important.

It has also been pointed out by Liebig, in his "Animal Chemistry," that the composition of the vegetable alkaloids approaches more

nearly to that of brain than that of any other class of compounds. As we cannot doubt that the action of these alkaloids on the system depends on their composition, it is not improbable, that, from their resemblance to brain in composition, they may take a share in the formation of nervous matter, which process they may promote or impede, according to the dose. In this manner we may conceive how it happens that that class of remedies, such as morphine, strychnine, quinine, &c., act directly on the brain and nerves, and even, as in the case of morphine, affect the powers of thought, which in a small dose it stimulates, and in a large dose altogether arrests; or, as in the case of strychnine, affect the nerves of motion, producing involuntary movements and convulsions.

Bones.—The bones of animals are composed of bone-earth and gelatinous tissue. By the action of hydrochloric acid the earthy matter is dissolved, and the animal tissue is left. It is soft, retains the form of the bone, and when dried becomes brittle and semitransparent. When boiled with water, it yields a solution of gelatine, fatty matter remaining undissolved.

The earthy matter is formed of a peculiar phosphate of lime, $8\text{CaO} + 3\text{P}_2\text{O}_5 = \text{HO}, 2\text{CaO}, \text{P}_2\text{O}_5 + 2(3\text{CaO}, \text{P}_2\text{O}_5)$; that is, a compound of two forms of tribasic phosphate, and also a considerable quantity of phosphate of magnesia. Burnt bones also contain soda; but it is not yet known whether it occurs originally in the form of soda-phosphate of magnesia, or as chloride of sodium. The earthy matter forms rather more than half the weight of the bone, and contains a variable proportion of carbonate of lime. Fluoride of calcium is always present in recent bones; in fossil bones, and in human bones from Herculaneum it is also found. Fluoride of calcium is more easily detected in fossil than in recent bones, but Daubeny has proved it to be present in all bones. It amounts sometimes to 10 or 12 per cent. of the earthy part, but is generally in a much smaller proportion.

Teeth contain the same ingredients as bones, but the proportion of earthy matter is greater, amounting to nearly 70 per cent. The *enamel* of the teeth contains no animal matter, and fluoride of calcium is found in it.

In rickets the proportion of earthy matter is much diminished. Callus and exostosis are said by Valentin to contain more carbonate of lime than sound bone, and carious bone to contain less. Schmidt has recently described a case, originating in mental distress, in which, from the accumulation of free acid in the fluids, all the bones were gradually deprived of their earthy part, which was dissolved by the acid, and were reduced to the state of soft flexible masses. The disease was ultimately fatal. It is probable that the free acid was that of the juice

of the muscles, which, in consequence of some morbid condition, was enabled to pass through the membranes which usually confine it.

When bones are heated in the open fire they leave an earthy skeleton, which is quite white, and has the form of the bone. If bones are heated in close vessels, they give off carbonate of ammonia and tarry products, and leave a black mass, which consists of bone-earth, with about 10 per cent. of finely divided charcoal. It is called bone or ivory-black, and is much used to decolorize organic solutions.

ANIMAL SECRETIONS AND EXCRETIONS.

Milk.—This important secretion, destined for the support of the young of the mammalia, is characterized by the caseine it contains. But it also contains certain oily or fatty matters which constitute butter, and which, besides fats analogous to the ordinary animal fats, contain compounds of glycerine with certain volatile acids (see p. 1063), to which the smell and peculiar taste of butter are owing. Milk further contains sugar of milk, or lactine (see p. 970); and, when the caseine has been coagulated by an acid, the whey, besides lactine and salts, contains an albuminous matter, which is coagulated by heat. It is important to observe that lactine occurs in the milk of the carnivora, although their food contains neither starch, sugar, nor gum, but is composed of albuminous matters and fat. (Bensch.)

The composition of milk is such, that it is capable of supporting animal life without any other food. Its caseine and albumen serve for the formation of blood and for the nutrition of the animal tissues, while its sugar and fat support respiration; and it furnishes, besides, all the salts which the body requires.

The following table exhibits the composition of the milk of woman, of the ass, and of the cow. (Henry and Chevalier.)

	Woman.	Milk of Ass.	Cow.
Cheese or Caseine	1·52	1·82	4·48
Butter	3·55	0·11	3·13
Sugar of Milk	6·50	6·03	4·77
Salts and Mucus	0·45	0·34	0·60
Water	87·98	91·65	87·02
	100·00	100·00	100·00

The analysis of the milk of two bitches, fed exclusively on flesh during five days, yielded, according to Bensch —

	I.	II.
Water	77·52	75·54
Butter	10·95	10·75
Sugar of Milk or Lactine, and soluble salts	3·19	3·47
Cheese and insoluble Salts	8·34	10·24
	100·00	100·00

When the food is highly farinaceous, the proportion of butter is increased; but when the food contains much of the albuminous compounds, there is less butter and more caseine present. The more active exercise is taken, the smaller also is the proportion of butter.

Milk, after it has become sour, undergoes the vinous fermentation.

The acid of sour milk is the lactic, formed by the lactic fermentation from a part of the sugar of milk or lactine. This peculiar fermentation depends on the presence of caseine in a certain state of decomposition, and is not confined to sugar of milk; for cane sugar or grape sugar may equally be converted into lactic acid, by the addition of moist cheese or pressed curd (not salted), which has been exposed to the atmosphere. (See p. 986.) This fermentation succeeds best at a temperature a little above 90°, but it is speedily checked by the accumulation of free acid, unless the acid be neutralized by adding carbonate of soda from time to time, or by adding prepared chalk equal to half the weight of the sugar at the commencement of the process. It has been already mentioned, (pp. 987 and 1064,) that when the lactate of lime is formed, the prolonged contact of the caseous ferment produces, most readily at 100° to 105°, a second fermentation, in which butyric acid takes the place of the lactic acid, while carbonic acid and hydrogen are given off, and the lactic acid is entirely destroyed. This may be called the butyric fermentation.

Saliva.—This fluid, secreted by the salivary glands, is composed of water, with about 1 per cent. of solid matter, partly saline. It often contains a trace of sulphocyanide of potassium, or at least of a salt which strikes a red colour with persalts of iron; but this may be done by an acetate. The animal matter of saliva has been described under the name of *Salivary matter*. It is soluble in water, and not coagulated by heat.

Saliva possesses, in an eminent degree, the property of frothing with air, like a solution of soap; and Liebig (*Animal Chemistry*, p. 113) conceives that its use is to introduce in this manner, during mastication, a certain quantity of air into the stomach, the oxygen of which is employed in digestion.

Gastric Juice.—This remarkable fluid seems to contain hardly any principle capable of accounting for its solvent power. According to Wasmann and other chemists, it contains a peculiar principle, *Pepsine*, which has the property of dissolving food, and which is obtained by the action of water on the well-washed lining membrane of the stomach of the pig. According to Liebig, however, pepsine, as a distinct compound, does not exist. The solution of the lining membrane, slightly acidulated with hydrochloric acid, certainly dissolves albumen

and fibrine, if kept in contact with them out of the body at the ordinary temperature; but none of these effects take place unless the membrane has been previously exposed to the air, *and is in a state of decomposition*. Hence Liebig ascribes (Animal Chemistry, 109 et seq.) the solvent power of the gastric juice to the gradual decomposition of a matter dissolved from the membrane, aided by the oxygen introduced in the saliva. Albumen, &c., when thus in contact with decomposing or fermenting matter, are rendered soluble by a new arrangement of their particles. The accumulation of free acid at last puts a stop to further change. The whole food is now brought into the form of *chyme*, an opaque homogeneous fluid, which afterwards passes, first into *chyle*, and finally into perfect blood. In the chyle the formation of fibrine has already taken place; for, when drawn, it coagulates spontaneously, like blood.

When the gastric juice, after being mixed with water, is distilled, the distilled portion is found acid, from free hydrochloric acid, or, according to some chemists, from hydrochloric, acetic, and butyric acids; and it has been concluded that these acids exist free in the gastric juice. But Liebig has pointed out that we have good evidence of the presence of phosphoric acid in the gastric juice, and that the experiments of Lehmann prove also the presence of lactic acid, as the salt which he extracted and analyzed turns out to have been lactate of magnesia. Now, phosphoric and lactic acids being by much the least volatile, and also the most powerful of all the acids found in this fluid, it is evident that the result of distillation does not prove the presence of the volatile acids in the free state in the gastric juice, but rather that the free acids are phosphoric and lactic, which, when heat is applied, expel the weaker volatile acids.

The hydrochloric acid is consequently, in all probability, derived from the chlorides of potassium and sodium, and the acetic and butyric from acetates and butyrates.

But if the gastric juice contains free lactic and phosphoric acids, metallic chlorides, salts of organic acids, with the alkalies and magnesia, and if, as Tiedemann and Gmelin have shewn, the part of this juice soluble in alcohol is identical with the alcoholic extract of soup, or of the juice of flesh, it follows that the gastric juice must be very nearly identical in composition with the juice of flesh or fluid of the muscles. If this be so, we can easily see whence the stomach obtains a liquid of this kind, containing free acid, while the blood and chyle are alkaline. It is also quite conceivable that the juice of flesh, on the above supposition, may prove a valuable remedy in some of the commonest forms of dyspepsia.

It is not yet known whether the gastric juice contains kreatine ; but in the meantime it appears to be most consistent with the present state of our knowledge to ascribe the solution or digestion of the food in the stomach to the combined action of dissolved animal matter derived from the lining membrane, and in a state of change, along with free phosphoric and lactic acid.

Pancreatic Juice.—The fluid secreted by the pancreas is poured into the duodenum, and mixes with the chyme as the latter leaves the stomach. It contains albumen, and, according to some, caseine, and is acid. Its nature, however, is little understood, and its peculiar uses at present are unknown.

BILE AND BILIARY CALCULI.

The bile is a yellowish-green viscid liquid, secreted by the liver. It has a faint, disagreeable smell ; and its taste is at first sweet, afterwards bitter and nauseous. Ox bile has been chiefly examined, but that of man and other animals is very similar. The researches of Tiedemann and Gmelin, of Berzelius and of Demarçay, have shown that bile may be made to yield a vast number of different compounds, most of which are products of decomposition.

The bile, according to Demarçay, contains soda in combination with a peculiar acid, *choleic acid*. When bile is boiled with an excess of hydrochloric acid, it yields ammonia, *taurine*, and *choloidic acid* ; and, when boiled with caustic potash, it yields carbonic acid, ammonia, and *cholic acid*.

Choleic Acid.—When bile is acted on by alcohol, certain impurities are left undissolved. The purified bile gives with acetate of lead a precipitate of choleate of lead, which, when acted on by sulphuretted hydrogen, yields choleic acid.

It forms a yellow spongy mass, soluble in water and alcohol, which has an acid reaction and a bitter taste, and is decomposed by heat. It combines with soda, forming a compound which Demarçay considers as a soap, the solution of which in water has the physical characters of bile.

It can no longer be doubted that bile is truly choleate of soda, for Verdeil has recently succeeded in obtaining bile in the crystallized form, and with the composition of choleate of soda. Ox bile is dried up in the water-bath, and the residue acted on by 20 parts of absolute alcohol. The solution is filtered from the mucus, and digested with blood-charcoal, which renders it quite colourless. Ether is then added till the whole becomes slightly milky, and, on standing, the pure

crystallized bile is deposited in small acieular crystals. The formula of these crystals is $\text{NaO} + \text{C}_{44}\text{H}_{40}\text{NSO}_9$. (Verdeil.)

Choleic acid is $\text{HO}, \text{C}_{44}\text{H}_{40}\text{NSO}_9$, and this represents the organic part of the bile. The presence of sulphur in it, to the extent of nearly 4 per cent., was overlooked till very recently, when Redtenbacher discovered that taurine, which is derived from it, contains 38.4 per cent. of sulphur, also previously overlooked. Since this remarkable discovery, the composition of the other bodies derived from choleic acid has not been again ascertained, nor their relation to the new formula of choleic acid accurately fixed. It is, therefore, impossible at present to give, as in the last edition of this work, equations representing the results of the decomposition of choleic acid by acids.

When choleic acid is boiled with hydrochloric acid, it yields ammonia, taurine, and choloidic acid. The latter, being insoluble, is deposited, and the taurine is extracted from the mother-liquor by concentrating and adding a large quantity of alcohol, when the taurine slowly crystallizes.

Choloidic Acid.—This acid is solid, fusible, of a yellow colour, resinous aspect, and bitter taste, insoluble in water, soluble in alcohol. It combines with bases, neutralizing them, and forming salts which are soluble in alcohol. It contains no nitrogen, and its formula is $\text{C}_{60}\text{H}_{50}\text{O}_{11}$. (Theyer and Schlosser.)

The formula just given for choloidic acid is that deduced by Theyer and Schlosser from their analyses, which were made, however, before the discovery of the presence of sulphur in choleic acid; and although it enabled them to give an equation for the process in which choloidic acid and taurine are formed, this cannot yet be done with the present formula of choleic acid. Besides, these chemists in their equation make no reference to ammonia, which is said by Demarçay to be formed along with choloidic acid and taurine, and which is even mentioned in their own experiments: For the present, therefore, we can only state, that, when boiled with acids, bile (choleate of soda) or free choleic acid is resolved into choloidic acid, taurine, and ammonia.

Dyslysine.—When the boiling of bile with hydrochloric acid is very long continued, the choloidic acid is gradually, but at last completely, converted into a substance of similar aspect, but insoluble both in water and in alcohol. This is called *Dyslysine* by Berzelius, and it has been shewn, by Theyer and Schlosser, to differ from choloidic acid only in containing 4 eq. of water less. Its formula, therefore, is $\text{C}_{60}\text{H}_{46}\text{O}_7$.

Action of Nitric Acid on Choloidic Acid.—This action has recently

been studied by Redtenbacher, who has shewn that a great variety of products are the result. Some of these are volatile, namely, acetic, butyric, valerianic, caprylic, and capric acids; along with which a heavy oil distils over, which by contact with alkalis is resolved into a new acid, *nitrocholic acid*, and a neutral oil, *cholacrole*. The other products are fixed, namely, a new resinous acid, *choloidanic acid*, and a second new acid, also resinous, *cholesteric acid*.

Volatile Acids.—These, as far as they go, are identical with the volatile acids formed by the action of nitric acid on oleic acid. It is probable that the other volatile acids of the series $(CH)_n + O_4$, which occur in the case of oleic acid, are also produced in this case, but could not be detected from the smallness of their quantity and the similarity in their properties. But the formation even of those obtained by Redtenbacher is highly important, as proving the existence of a close relation between bile and the fatty acids.

Heavy Volatile Oil. Nitrocholic Acid.—When the volatile products are rectified, this oil falls to the bottom of the vessel. It is washed with water, to remove the acids, and then forms a clear oily liquid, nearly or quite colourless, of a most pungent and stupefying odour, evidently poisonous. By the contact of potash it is decomposed, being resolved into nitrocholic acid and cholacrole. The new acid combines with the potash and forms a salt which crystallizes in large sulphur-yellow crystals. This salt explodes when heated, and is decomposed by sulphuric acid, nitrous acid, and hydrocyanic acid being given off. Its formula is $C_2HN_4O_9, KO$; and the nitrocholic acid is $C_2HN_4O_9, HO$.

Cholacrole.—This is a neutral oil, having, like the preceding, a terribly pungent odour, but not so stupefying, and somewhat analogous to that of cinnamon. It is decomposed with a slight deflagration when heated to 212° . Its formula is $C_8H_5N_2O_{13}$. Both this and the preceding substance are evidently coupled or conjugate compounds, containing nitric or nitrous acid.

Fixed Products. Choloidanic Acid.—This acid is found in the retort as a frothy mass of crystals, floating on a brown, acid, bitter liquid. It is purified by solution in hot water, which deposits it in white, slender, hair-like prisms, very light and bulky. It is soluble in alcohol. Its salts do not crystallize, and most of them are insoluble. Its formula is $C_{16}H_{12}O_7 = C_{16}H_{11}O_6, HO$; but this formula has not been controlled by the analysis of any salt.

Cholesteric Acid.—This acid is found in the brown acid liquid, on which the preceding acid floated, along with a soft resinous matter, apparently imperfectly oxidized choloidic acid, and oxalic acid. The

resin is separated by adding water, which causes it to be deposited, filtering, evaporating, and again adding water, and repeating the process till the addition of water no longer causes turbidity. The liquid is then neutralized with ammonia, and precipitated by nitrate of silver. The precipitate, consisting of oxalate and cholesterate, is next boiled in water, which dissolves the latter salt, and on cooling deposits it in crystals. This salt is decomposed by sulphuretted hydrogen, and the acid thus obtained in solution. It dries up into a gummy mass, and does not crystallize. Its formula is $C_8H_4O_4.HO$. None of its salts, except that of silver, are crystallizable, and those of the earths and metallic oxides are insoluble.

Redtenbacher has also shewn that cholesteric acid is the chief product of the action of nitric acid on cholesterine, hence its name.

Taurine.—This substance forms white crystalline needles, which are soluble in water, and sparingly soluble in alcohol. Its formula is $C_4H_7NS_2O_6$.

The presence of sulphur in taurine, to the amount of 38.6 per cent., had long been overlooked, till it was discovered by Redtenbacher. It is very remarkable, that a compound of a nature so complex as taurine should yet be so very permanent that it is not decomposed even by strong nitric acid. The form of combination in which the sulphur exists in taurine is not known, but it appears not to be oxidized. It is probable that taurine is a coupled or conjugate compound. Its formation cannot at present be so explained as to be represented in an equation.

Von Gorup Besanez has observed that when bile is left to itself it undergoes spontaneous decomposition, the mucus acting as a ferment. The products of the fermentation are the same as are formed when bile is boiled with acids, namely, choloidic acid, ammonia, and taurine. He even recommends this as the best method of obtaining taurine.

Cholic Acid.—This acid is formed, along with carbonic acid and ammonia, when bile or choleic acid is boiled with an excess of caustic potash. It is precipitated by acetic acid, and purified by alcohol from unaltered choleic acid.

When pure, it forms fine needles, which are permanent in the air; or large tetraedrons, which become opaque on exposure. It is insoluble in water, soluble in alcohol and ether. It forms neutral salts with bases. Its formula is said to be $C_{42}H_{32}O_8.HO$; but its formation cannot be represented in an equation, until it be ascertained what becomes of the sulphur of the choleic acid of the bile. It is evident that either some other compound must be formed, in addition to cholic

acid, carbonic acid, and ammonia, or else that cholic acid contains all the sulphur of the choleic acid.

Schlicper has shewn that cholic acid is converted by the action of nitric acid into products the chief of which is cholesteric acid. This fact is important, as, in conjunction with the experiments of Redtenbacher, establishing a near relation in constitution between choloidic acid, cholesterine, and cholic acid, all of which, when acted on by nitric acid, yield cholesteric acid.

Berzelius states that the bile is far from being so simple in its constitution as Demarçay supposes; and by a series of ingenious processes has obtained from the bile a number of different substances, which he has named *Biline*, *Biliverdine*, *Dyslysine*, *Fellinic acid*, and *Cholinic acid*, besides taurine and cholic acid, as already described. Biline is essentially the same as Demarçay's choleic acid, and it is probable that most of the others are products of decomposition. But even supposing choleic acid to be composed of two or more different compounds, not isolated by Demarçay, yet, as Liebig has well remarked, (Animal Chemistry, 315,) we must not overlook the fact, that it is constant in its composition, and that from this composition we can deduce the principal products of the action of acids and alkalies on bile. It is choleic acid or bile *as a whole*, whether it be one compound or a mixture of several, to which we have to look for the explanation of the changes by which bile may be formed or decomposed. The researches of Berzelius at one time rendered it probable that choleic acid is not a single compound; but this does not affect its ultimate composition, nor its relation to decomposing agents; and the most recent experiments, especially that of Verdeil, who obtained choleate of soda crystallized, have established the simpler view. It is also clear that bile is very prone to change in almost all circumstances, and yields a great variety of products, most of which have little physiological interest. For these reasons we shall merely refer the reader to the elaborate paper of Berzelius in the foreign journals. The results of Demarçay we have given more in detail; because, as calculated and interpreted by Liebig, and confirmed by Theyer and Schlosser, Verdeil, Redtenbacher, and other chemists, they admit of direct application to physiology.

When dried bile is acted on by alcohol, the pure bile or choleate of soda is dissolved, and the residue is found to contain mucus, salts, and fatty matter. The latter consist of cholesterine and ordinary fat, and possibly contain a portion of the peculiar fats of brain. The dissolved portion, besides true bile, contains a small portion of soaps of margaric and oleic acids with soda.

The sugar of bile or picromel of Gmelin, so called from its sweet and bitter taste, appears to be choleic acid or biline, altered by the processes to which it has been subjected.

The bile serves important purposes in the animal economy. It was long viewed as an excretion, and supposed to be expelled in the fæces; but Liebig shewed that the normal fæces contain no bile, and that, therefore, in passing through the small intestine and the upper part of the large intestine, it must be reabsorbed, and serve other purposes. As it is poured into the chyme immediately after that mixture leaves the stomach, it probably aids in the process of digestion and nutrition; but it certainly also undergoes oxidation or combustion ultimately, and the greater part of its carbon and hydrogen are given out as carbonic acid and water by the lungs, their combustion having served to keep up the animal heat. The rest of its carbon and hydrogen, with its nitrogen, sulphur, and soda, are expelled in the urine, no doubt after contributing to support some of the vital processes. We shall return to this subject when treating of the vital processes of the animal organism.

The preceding statements apply strictly to ox bile, but it has been ascertained that human bile, as well as the bile of other animals, agrees entirely with ox bile in its properties, composition, and products of decomposition.

With regard to the formation of bile, it is apparently produced in a different way in herbivorous and in carnivorous animals. In the former, the quantity of bile is very large, and there can hardly be a doubt that the non-azotized part of their food takes the chief share in its formation. In the latter the amount of bile is very much smaller, and as their food contains no non-azotized matter except fat, the bile must either be formed from the albuminous compounds alone, or with the aid of fat.

Biliary Calculi.—The concretions which form in the gall-bladder, and are often the cause of much suffering, are almost always composed of cholesterine, with more or less colouring matter. Hot alcohol dissolves the cholesterine, and deposits it in shining scales on cooling. These calculi have often a form nearly cubical, and a pearly lustre. For the properties and composition of cholesterine, see p. 1125.

Lithofellic Acid.—This acid has recently been discovered by Goebel in a biliary concretion, and appears to be the chief constituent of the concretions called *bezoar stones*, which occur in herbivorous animals. According to Ettling and Will, its formula is $C_{40}H_{36}O_8 = C_{40}H_{35}O_7.HO$. It is soluble in hot alcohol, and forms a crystalline powder on cooling. It is insoluble in water, and forms with alkalies

soluble soaps, with oxides of lead and silver insoluble compounds. It is decomposed by heat, and when acted on by nitric acid yields a new coupled acid, the formula of which is $C_{40}H_{23}NO_{11}$. When distilled, lithofellic acid loses 2 eq. of water, and yields pyrolithofellic acid $C_{40}H_{34}O_6 = C_{40}H_{33}O_5 \cdot HO$.

Excrements.—The excrements of man contain about one-fourth of their weight of solid matter. The ashes of dry fæces amount to 13.58 to 15.00 per cent., and are chiefly composed of earthy phosphates and other insoluble salts. The excrements also contain nitrogen, and yield ammonia when they putrefy. The value of night-soil as manure depends on the salts and ammonia of the fæces, and also in a great measure on the ammoniacal and other salts of the urine. The colour of fæces is generally said to be owing to bile; but Liebig states that there is only a mere trace of bile, if any, to be found in the fæces either of man or animals. The yellow matter of fæces is insoluble in alcohol, with the exception of a small proportion, and even that has not the characters of bile.

Liebig has recently observed that if albuminous compounds, such as albumen, fibrine, caseine, or gelatine, are melted with solid hydrate of potash, and the heat continued till the greater part or the whole of the nitrogen has been dissipated as ammonia, and hydrogen begins to be given off, the residue, when supersaturated with diluted sulphuric acid, and distilled, yields an acid liquid, possessing in a very intense degree the peculiar and characteristic odour of human fæces. The odour varies according to the substance employed, and in this way all the varieties of fæcal smell may be obtained. As the action of caustic potash at a high temperature is simply a limited or incomplete oxidation or combustion, this observation shews that the view taken by Liebig in his "Animal Chemistry," five or six years ago, of the nature of fæces, was correct. He considered the fæces to represent the imperfectly burned or oxidized portions of the food, and compared it to the soot or lamp-black in an ordinary furnace.

It is worthy of notice that the excrementitious matters, whether solid or liquid, of the animal body, contain, besides the imperfectly burned organic substances, the ashes or inorganic substances of the food. The soluble phosphates, sulphates, and chlorides are excreted in the urine, but the insoluble phosphates, sulphates, and silica are expelled in the fæces. In both cases, the composition of the ashes must vary according to the nature of food, and can only be uniform, when no change of diet is permitted.

It is probable that the fætid compounds above mentioned, as possessing characteristic fæcal odours, are of an acid nature, or at least

contain volatile acids. They would seem also to be volatile, and are well worthy of investigation. The study of them will certainly lead to valuable results. It is already known that caprylic acid, one of the volatile acids of butter, has a strong odour of sweat, and that valerianic acid, an acid belonging to the same series, has an unpleasant smell, somewhat analogous to that of fæces in certain states. It has further been shewn by Liebig that valerianic acid and butyric acid, both acids of the same series, that of $(\text{CH})_n + \text{O}_4$, are actually formed, along with tyrosine and leucine, when caseine is heated with caustic potash, when the action is not carried so far as in the process just described. Liebig states that these acids are formed from the leucine. (See Leucine.)

When the food contains more of the non-azotized constituents than the system can oxidize, these constituents appear unchanged in the fæces, if insoluble in water. Thus, when the food contains too much starch, the fæces are full of starch granules. (Liebig.)

It has been supposed by some that the fæces, in the normal state, and even before they are expelled, are in a state of putrefaction or fermentation. But this is not the case. Putrefaction does not occur in the fæces till after exposure to the air. After this, they enter into fermentation or putrefaction, and are found capable of exciting the vinous fermentation in a solution of sugar.

Lymph.—The lymph of cellular membrane is water, with a small trace of albumen and of common salt. The lymph secreted by the serous membranes is much more highly charged, containing 7 or 8 per cent. of albumen and salts. It coagulates when heated, or by the action of nitric acid. The liquor amnii and the fluid of hydatids is similar; but the fluid of dropsy is said to contain urea, and to have cholesterine suspended in it.

Mucus.—This is the secretion of the mucous membranes. When dried, it leaves 6 or 7 per cent. of yellowish solid matter, of which about 5 parts are mucus, the remainder albumen and salts. Mucus does not dissolve in water, but swells like tragacanth into a viscid mass. It dissolves in caustic potash.

Pus is the matter secreted by ulcerated surfaces. When healthy, it is a thick yellowish liquid, formed of opaque globules floating in a clear fluid. When mixed with water, the globules fall, forming a yellow insoluble sediment. Pus contains about 14 per cent. of solid matter, and is coagulated by heat and by acids. It contains albuminous matter, fatty matter, and salts.

The matter of the globules of pus is similar to that of the globules of blood, or globuline. Pus is distinguished from mucus by the

microscope, or by the action of caustic potash, with which pus becomes thick and ropy, while mucus forms a thin solution.

URINE AND URINARY CALCULI.

Urine.—This important excretion is separated from the arterial blood in the kidneys. It has a pale yellow colour and a peculiar smell. Its density varies from 1.012 to 1.030. It has an acid reaction, or is neutral, and even sometimes alkaline in a state of health.

On standing it deposits a slimy mucus-like substance, secreted from the lining surface of the bladder. This mucus acts as a ferment, and causes the urine after a time to undergo decomposition; for, when it is separated by the filter, the urine may be kept unchanged for a much longer time.

When spontaneous decomposition has taken place, the urine is alkaline from the presence of carbonate of ammonia, derived from the urea. Urine contains about 7 or 8 per cent. of solid matter, the remainder being water.

The characteristic organic principles of urine are urea and uric acid. The urea has been recently declared by Cap and Henry to be combined with lactic acid; but, in repeating their experiments, Gregory has always obtained pure urea instead of the lactate; and Pelouze, as well as many other chemists, have obtained the same result. If lactic acid ever occurs in urine, it is probably an abnormal product, for Liebig has proved, by experiments on a very large scale, that normal urine, whether fresh or putrid, contains no lactic acid. It is not known precisely in what state of combination the uric acid occurs; but, when it is not deposited spontaneously, it appears on the addition of an acid, and the spontaneous deposition of it is probably owing to the presence of free acid in unusual quantity.

The proportion of urea has been found by Lecanu to be tolerably uniform in the same individual, but to vary much in different persons. It is larger in adult men than in women, and least of all in old people and very young children. The proportion of uric acid varies in a similar way. The following analysis of urine, by Berzelius, will give a view of the usual composition of human urine; bearing in mind that what in this analysis is called lactic acid and lactates is not so, but consists chiefly of organic matter, the precise nature of which is not yet ascertained, but which, as is now known, contains both kreatine and kreatinine. Liebig has recently discovered that human urine always contains hippuric acid, in quantity equal to that of the uric acid; that both these acids are more soluble in a solution of phos-

phate of soda than in water, and that this solution has an acid reaction. To this he ascribes the acid reaction of the urine. He has also found that putrid urine, when distilled with a fixed acid, yields acetic acid in considerable quantity. This last observation had been made in 1820 by Proust. The acetic acid is accompanied by a resinous azotized substance, and Liebig considers both to be products of the decomposition of the colouring matter of the urine:—

Water	933.00
Urea	30.10
Uric Acid	1.00
Lactic Acid, Lactate of Ammonia, and Animal Matter adhering to them	17.14
Mucus of the Bladder	0.32
Sulphate of Potash	3.71
Sulphate of Soda	3.16
Phosphate of Soda	2.94
Phosphate of Ammonia	1.65
Chloride of Sodium	4.45
Hydrochlorate of Ammonia	1.50
Earthy Matters, with a trace of Fluoride of Calcium	1.00
Siliceous Earth	0.03
	1000.00

Scharling has recently examined the brown organic matter which gives the colour to inspissated urine, and seems also to be the source of its peculiar odour. He obtained a brown fusible resinous mass, having a strong odour of castoreum when dry, and a urinous smell when boiled with water. He calls it *oxide of omichmyle*, (from *ουριχμια*, urine,) and supposes it to contain a radical, omichmyle, the composition of which is still unknown.

When urine is distilled with an excess of nitric acid, there are formed several products, among which Scharling states that he has observed benzoic acid, and an acid containing chlorine derived from the salts of the urine. This acid appears also to be formed when oxide of omichmyle is distilled with nitromuriatic acid. From his analysis Scharling deduces the formula $C_{14}H_4ClO_3 + HO$, which represents benzoic acid in which 1 eq. of hydrogen is replaced by 1 eq. of chlorine. It is also isomeric with chloride of salicyl or chlorosalicylic acid. The presence of benzoic acid in putrid urine was observed by Proust, and it is obvious that its source is the decomposition of hippuric acid.

Along with this acid there is formed a volatile greenish-yellow oil, which Scharling found to contain twice as much chlorine, and the elements of nitric acid. This compound he calls nitro-chloromichmyle. When heated with acids it is decomposed, and yields another oily matter, chloromichmyle. All these observations require confirmation.

Pettenkofer has recently observed that urine contains a substance which yields with chloride of zinc a crystalline compound nearly inso-

luble in cold water. The method of preparing Pettenkofer's compound has been described already, (see p. 1217,) and it has been mentioned that the organic ingredient of this compound, which in Pettenkofer's analysis yielded the formula $C_8N_3H_8O_3$, has been shewn by Liebig to be a mixture of two compounds, namely, kreatine $C_8N_3H_{11}O_6$, and kreatinine $C_8N_3H_7O_2$. A mixture of 1 eq. of the former to 3 eq. of the latter has exactly the composition represented by Pettenkofer's formula. It is only the kreatinine which combines with chloride of zinc; but the compound is mixed with crystals of free kreatine, which is but sparingly soluble in cold water.

It is evident that the chemistry of urine is still very imperfect, since no analysis yet made has taken account of the hippuric acid, kreatine, and kreatinine. Moreover, the nature and composition of the substance or substances to which are owing the peculiar colour and odour of urine are almost entirely unknown.

We know, however, that the urine is the vehicle by which all the soluble salts of the food, or that may be formed in the body, are expelled, and that the superfluous nitrogen is also excreted in the urine in the form of urea and ammoniacal salts.

The nature of the salts in the urine is entirely accidental, or, in other words, dependent on that of the inorganic constituents of the food; and it has been shewn by Liebig that normal urine may be acid, neutral, or alkaline. It always becomes alkaline when the food contains salts of soda or potash with organic acids. These acids are oxidized in the circulation, yielding carbonic acid, which unites with the alkalies, and the alkaline carbonates appear in the urine. When the food contains but very little of such salts of organic acids, the urine may be neutral; and when it contains none at all, the urine becomes acid, from the solution of uric or hippuric acid, or both, in phosphate of soda. It is evident that by a judicious choice of diet we can bring the urine, without injury to the health, into any state that may be wished; a most valuable fact in reference to the treatment of calculous diseases.

When a man drinks within a short time several glasses of a very weak saline solution such as many mineral springs afford, he can take a very large quantity, (some people have taken 20 quarts,) the liquid being rapidly absorbed by endosmose, and expelled by the kidneys, so that in a few hours the urine may be rendered colourless and almost identical with the spring-water consumed. But if he drink a solution as strong or only a little stronger than the blood is in salts, no absorption takes place, and the stomach becomes so loaded that it is found impossible to persevere in drinking such a solution. If, again, the

solution be much stronger than the blood, exosmose takes place, and the water of the blood passes into the stomach and intestinal canal, producing watery alvine evacuations. This is the true explanation, a mechanical one, of the purgative action of neutral salts. If a piece of membrane, such as fresh bladder or gut, be sprinkled with salt, it is soon found shrivelled and swimming in brine, which, when of a certain strength, runs off its surface, as water does off that of fat.

An artificial urine may be formed, according to Liebig, by dissolving in 1 lb. of hot water 40 grains of dry phosphate of soda, $\text{PO}_5, 2\text{NaO}, \text{HO}$, or 90 grains of the crystallized salt $\text{PO}_5, 2\text{NaO}, \text{HO} + 24 \text{ aq.}$; and then dissolving in the alkaline solution thus formed 15 grains of uric acid, and 15 grains of hippuric acid. On cooling, and after standing for some time, $7\frac{1}{2}$ grains of uric acid, or acid urate of soda, are deposited, precisely similar in form and aspect to the uric acid deposit in urine. $22\frac{1}{2}$ grains of the organic acids remain dissolved, and the solution has now a strong acid reaction. The addition of an acid causes a precipitate of uric acid, as in real urine.

The urine of the herbivora is alkaline, and, when the animals are stall-fed, contains, beside urea, a considerable quantity of hippuric acid; but when they live in the open air, or are forced to labour, benzoic acid alone is found.

The urine of the carnivora is acid, and contains phosphates and sulphates of ammonia and soda, as well as uric acid and urea.

The urine of serpents and of birds is of a soft semisolid consistence, and dries into a mass like chalk. It is almost pure urate of ammonia, but contains a small quantity of phosphates.

Urinary Calculi.—The most abundant calculi are those of *uric acid*. They have generally a fawn colour, are soluble in caustic potash, and precipitated from the solution by acids. They also dissolve in nitric acid with the aid of heat; and the solution, when gently evaporated to dryness, leaves a purple stain of murexide. This species of calculus is totally consumed before the blowpipe, leaving a mere trace of ashes. It has been proposed to dissolve uric acid in the bladder by weak alkaline injections, and also by the administration of citrates, tartrates, &c. of the alkalies, which cause the urine to be alkaline from alkaline carbonates. But these methods have not succeeded. It is probable that the internal use of a weak solution of phosphate of soda, as proposed by Liebig, may be more successful.

It is very interesting to observe that uric acid calculus is said to be unknown, except in imported cases, in the Rhine district. The cause of this immunity is that the people use as their habitual beverage the inferior Rhenish wines, which contain much tartar, and only 5 or 6 per

cent. of alcohol, and consequently yield an alkaline, or at least a neutral, not an acid, urine. On the other hand, uric acid calculus prevails extensively among those of the higher classes who take little exercise, and drink the strong dry wines of Spain and Portugal, which contain hardly any tartar, and 12 or 14 per cent. of alcohol, circumstances favourable to imperfect or deficient oxidation.

This calculus is very common among the peasantry near Norwich, and also among those near Aberdeen. We are not informed as to any peculiarity of diet in Norfolk; but in Aberdeenshire the diet of the peasantry consists almost exclusively of oatmeal and cabbage, which diet is unfavourable to perfect oxidation and has a powerful tendency to produce acid urine.

Urate of ammonia occasionally forms a calculus, which is distinguished from the former by giving out ammonia when digested with potash. The same solvents apply here as in the last-mentioned calculus.

Bone-earth forms a common calculus, which is earthy, soluble in diluted acids, except acetic acid, insoluble in potash, and indestructible by heat. It is formed when the urine is alkaline, and of course can only be dissolved, if at all in the bladder, by rendering the urine acid.

Ammoniaco-magnesian phosphate also occurs pretty frequently. It is the same double salt which forms whenever magnesia, phosphoric acid, and an excess of ammonia are brought together. It is soluble in acetic acid, and precipitated again by ammonia. It has often a crystalline aspect. When heated, it gives off ammonia, and leaves phosphate of magnesia.

Fusible Calculus.—This very common calculus is a mixture of the two preceding. It is white and chalky, and melts easily before the blowpipe. Acetic acid dissolves part of it, hydrochloric acid the rest. This and the preceding calculus are, like bone-earth, soluble in acids.

Oxalate of lime, or *Mulberry calculus*, has a dark-coloured rough surface, and is very hard. It is insoluble in acetic acid; but, when heated to redness, it is converted into carbonate of lime, which dissolves in acids with effervescence. Its origin is the imperfect oxidation of uric acid, and it is therefore apt to appear in those affected with uric acid calculus, when they adopt any change of life favourable to oxidation, yet not sufficiently so to oxidize completely the uric acid.

Xanthic oxide is a rare calculus, first observed by Dr. Marcet. It has a light brown colour, and becomes resinous by friction. It dissolves in caustic potash, and is precipitated from the solution by carbonic acid. It dissolves in nitric acid without effervescence; and, when evaporated, leaves a yellow mass. Its formula is $C_5H_2N_2O_2$. (See p. 802.)

Cystic oxide is also very rare. Discovered by Wollaston. It is yellowish-white and crystalline, with a waxy lustre. It dissolves in caustic potash, and is deposited from the solution in hexagonal plates on the addition of acetic acid. It also dissolves in ammonia and the mineral acids; with the latter it forms crystalline compounds. When its solution in potash is heated, ammonia is first given off, and afterwards a combustible vapour, with the odour of sulphuret of carbon. Its formula is $C_6H_6NS_2O_4$. (See p. 802.)

Both the preceding species are entirely consumed before the blow-pipe.

Calculi sometimes occur, in which layers of uric acid alternate with layers of phosphate of lime, ammoniaco-magnesian phosphate, and fusible calculus.

CHANGES WHICH OCCUR DURING THE LIFE, GROWTH, AND NUTRITION OF VEGETABLES AND ANIMALS.

When we consider that the food of vegetables and of animals is either altogether different from their substance, or passes, before being assimilated, into a new form, we cannot hesitate to admit that the nutrition and growth of both classes of organized beings depend on chemical agencies, although these operate under peculiar conditions, and are influenced by the unknown force which we call Vitality, so as to produce results that cannot be imitated by the chemist in his experiments on dead matter.

It is true that we are able, by chemical means, to produce artificially a large number of compounds belonging both to the animal and vegetable kingdoms, such as urea, sarcosine, kreatinine, glycocoll, formic, oxalic, benzoic, salicylic, butyric, valerianic, caproic, caprilic, capric, margaric, lactic, and succinic acids, oil of garlic, oil of mustard, &c., besides many substances of properties and composition analogous to the above, which are not yet known to occur as natural products. But it must be observed that chemistry not only cannot produce an organized tissue, but has not yet discovered the means of forming the substances out of which tissues are constructed, such as cellulose, lignine, albumen, fibrine, gelatine, &c. Moreover, the greater number of these substances cannot be formed except from organic compounds, so that it is doubtful whether we could produce any of them if confined, as vegetables are, to the inorganic forms of matter. Again, the greater number of artificial organic products are such as are formed in nature by the destruction of more complex substances, and very frequently

they are such as are destined to excretion, and are really the *débris* of effete tissues, hardly entitled to the name organic.

At the same time it must be admitted that the number of substances connected with the organic world which can be formed artificially is rapidly increasing, and that our new methods approach far more nearly in their principles, as well as in their results, to the processes of organic life, than was supposed possible a few years since. It is now quite conceivable that we may discover the means of producing, for example, a body having the composition and chemical properties of albumen or gelatine. But there is no reason, derived from the present state of our knowledge, for thinking that we shall ever be able to give to such a compound the form of an organized tissue.

The first step in all organisms is the formation of a cell; and, although in Ascherson's celebrated experiment of placing albumen in contact with a fat oil, membranous sacs or cells, containing a liquid, and possessing the power of endosmose and exosmose, are formed, yet we cannot assume that these so-called cells are true cells such as compose organisms, and we must consider the formation of organized cells as, for the present, quite beyond our reach.

The food of vegetables, as far as their organic structure is concerned, consists entirely of inorganic compounds; and no organized body can serve for the nutrition of vegetables until it has, by the processes of decay or putrefaction, been resolved into certain inorganic substances.

These substances are carbonic acid, water, and ammonia, which are well known to be the final products of putrefaction. But, even where these are supplied to vegetables, their growth will not proceed unless certain mineral substances are likewise furnished in small quantity, either by the soil, or in the water used to moisten it. Almost every plant, when burned, leaves ashes, which commonly contain silica, potash, phosphate of lime; often also magnesia, soda, sulphates, and oxide of iron. These mineral bodies appear to be essential to the existence of the vegetable tissues, so that plants will not grow in soils destitute of them, however abundantly supplied with carbonic acid, ammonia, and water.

In the process of germination oxygen is absorbed, heat is given out, and in some cases at least an acid, said to be the acetic, is formed, the use of which appears to be to extract from the soil the bases necessary for the future progress of the plant. The starch or albumen of the seed becomes soluble, and in the juice undergoes certain changes, by which the woody fibre or lignine required for the stem and leaves is produced; but, as soon as leaves and roots are developed, the further

nutrition of the plant depends on their power of absorbing from the atmosphere and the soil the matters which constitute the food of the plant.

According to Liebig, (see his *Agricultural Chemistry*,) the whole of the carbon is now derived from carbonic acid, which is either absorbed from the atmosphere and rain-water by the leaves, or from the moisture and air in the soil by the roots. Its carbon is retained, and its oxygen given out; this decomposition being effected in the plant at all times when exposed to the action of light, along with a certain temperature.

It is probable that the fixation of carbon is a gradual process, having successive stages; that the carbonic acid is first reduced or deoxidized so far as to yield oxalic acid; thus, $C_2O_4 - O = C_2O_3$: that oxalic acid, with the aid of water, is farther reduced, so as to yield malic or citric or tartaric acid; thus, $C_4O_6 + 2HO = C_4H_2O_8$, and $C_4H_2O_8 - O_4 = C_4H_2O_4$; this last formula doubled is that of anhydrous malic acid, $C_8H_4O_8$. From this and similar compounds, sugar $C_{12}H_{12}O_{12}$, starch $C_{12}H_{10}O_{10}$, gum $C_{12}H_{10}O_{10}$, and woody fibre $C_{12}H_9O_9$ or $C_{36}H_{22}O_{22}$, are easily deduced, by the addition of the elements of water and the elimination of oxygen. Thus, 3 eq. hydrated malic acid, $C_{24}H_{18}O_{30}$, *plus* 6HO and *minus* O_{12} , is equal to 2 eq. dry sugar of grapes, $C_{24}H_{24}O_{24}$. There is good reason to think that the chief function of the alkalis in plants is to promote these metamorphoses.

The hydrogen and oxygen of vegetables are derived from water; and the reader will here observe, that the great mass of vegetables, consisting of lignine, starch, gum, &c., is actually composed of carbon *plus* water, or rather carbon *plus* oxygen and hydrogen in the proportion to form water.

The nitrogen of vegetables is derived chiefly, if not exclusively, from ammonia, which is supplied to them in rain. Liebig has shewn beyond all doubt that rain-water always contains more or less carbonate of ammonia. If we acidulate pure rain-water with a little sulphuric acid, and evaporate to a small bulk, the addition of lime causes the disengagement of ammonia, easily known by its pungent smell. It is remarkable that the ammonia of rain-water has always a putrid smell, which indicates its origin. In fact, it is derived from the putrefaction of preceding races of animals and vegetables, and must at all times exist in the atmosphere; although its relative quantity is so small, that it is not easily detected until it has been accumulated in rain, which, in passing through the air, dissolves it readily, and conveys it to the earth.

It is also to be observed that the soil itself, like all porous bodies, possesses the property of absorbing ammonia, and therefore will attract

it from the atmosphere. Alumina, peroxide of iron, and humus, all absorb ammonia powerfully. Gypsum (sulphate of lime) and other sulphates convert the carbonate of ammonia into the more fixed sulphate, which remains in the soil till absorbed by the roots. This explains in a great measure the use of these ingredients in fertile soils.

It is only under the influence of light that plants can decompose carbonic acid, fixing its carbon and setting free its oxygen. During the night, on the contrary, they undergo a kind of slow combustion, oxygen being absorbed, and carbonic acid formed. But the balance in this curious alternation is vastly in favour of the process by which oxygen is sent into the atmosphere, for, the whole carbon of a forest, for example, being derived from carbonic acid, an equivalent quantity of oxygen must have been liberated; and this consideration alone enables us to explain the fact, that, notwithstanding the enormous amount of oxygen withdrawn from the atmosphere by the respiration of animals, by combustion, by putrefaction, and by the action of vegetables during the night, in all of which processes the oxygen is converted into carbonic acid of equal volume, the proportion of oxygen in the atmosphere does not diminish, and that of carbonic acid does not increase.

From these considerations it appears that there must always exist a balance or fixed proportion between the existing amount of animal and that of vegetable life. Where animals abound, and where men carry on the usual operations of civilized life, there carbonic acid must be largely formed. But this carbonic acid, in yielding its carbon to vegetation, yields also its oxygen to restore the purity of the air, and support again the respiration of men and animals. Again, the decay and putrefaction of both animals and vegetables yield carbonic acid and ammonia, the very substances which form the food of a new race of vegetables; and these, again, contribute to the nourishment of new animals; so that, in this unceasing round of chemical changes, the death of one generation supplies the means of life to that which is to follow.

It has long been the prevailing opinion that the carbon of plants is derived directly from humus or humic acid existing in the soil, which is supposed to be absorbed in the form of a solution in water, or as humate of ammonia; but it must be admitted, as Liebig has shewn, that there is no evidence whatever that humus is directly absorbed by plants. Humus, as it exists in the soil, is almost entirely insoluble in water, and, when a soluble form occurs, the solution, however weak, is always of a dark brown colour; whereas the juices of plants, when first absorbed, are colourless. Again, humic acid, as described

by chemists, never occurs in soils, but is a product of the action of alkalies on humus, and, besides, forms solutions as dark-coloured as those of humus. Good fertile soil digested with cold water yields to it no colour; water, filtering through such soil, passes colourless, as may be daily observed; nay, moss-water, which is actually coloured brown by humus, is decolorized by passing through a good fertile soil containing humus; finally, a peaty soil, which contains more humus than any other, is notoriously barren.

On the other hand, the first vegetables which grew on the earth could not have derived their carbon from humus, which is a product of the decay of vegetables, but could only have obtained it from carbonic acid; and, if this source of carbon were then sufficient, there is no reason now to look for another. Besides, if we reflect on the extreme luxuriance of vegetation in uninhabited countries where the soil has never been manured, we cannot fail to perceive that the carbon of that vegetation must have been chiefly derived from the atmosphere; and when, in addition to this, we find that the proportion of humus in all soils bearing vegetation increases rather than diminishes, in spite of the vast amount of carbon annually accumulated and removed in the crops, we are compelled to adopt the same conclusion.

This latter consideration shews that the humus and other organic matters in manures do not act directly, at least to any great extent, in furnishing carbon, and that their use chiefly depends on other ingredients. These, as Liebig has demonstrated, are, first, the ammonia they contain or yield by putrefaction; and, secondly, the mineral bodies, such as potash, phosphate of lime, &c. found in their ashes.

But, although there is no evidence that humus is directly absorbed by plants, and the phenomena of peat and mossy soils prove that the soluble forms of the humus are unfavourable to vegetation, yet it cannot be doubted that the humus or mould, both of the soil and the manures, performs an important function. It slowly and gradually undergoes combustion, yielding a constant and steady supply of carbonic acid in moderate quantity. This is partly absorbed by the roots, and partly rises into the atmosphere to be absorbed by the leaves; but, as the proportion of humus in the soil does not diminish, that which is thus consumed is probably restored to the soil by the secretions or rather excretions from the roots, and from the decay of roots and leaves.

Humus also probably acts by absorbing and fixing the ammonia of the atmosphere.

The chief use of manures is, according to the above views, which have been admirably laid down by Liebig in his "Agricultural Chemistry," not to supply plants with carbon, but with inorganic matters, such

as the alkalies, lime and magnesia, chlorides, phosphates, sulphates, and silicates, and also with ammonia. Every plant requires certain mineral substances, without which it cannot prosper; and a soil is fertile or barren for any given plant, according as it contains these. Thus, the ashes of wheat-straw contain much silica and potash, while the ashes of the seeds contain phosphate of lime and phosphate of ammonia and magnesia. Hence, if a soil be deficient in any one of these, it will not yield wheat. On the other hand, a good crop of wheat will exhaust an average soil of these substances, and it will not yield a second crop till they have been restored, either by manure or by the gradual action of the weather in disintegrating the subsoil. Hence the benefit derived from fallows and from the rotation of crops.

Again, all seeds and many roots, and indeed all esculent vegetable products, contain much of the albuminous matters. But these matters contain, as essential to their existence, alkaline and earthy phosphates, and sulphur. Hence, a fertile soil must always contain phosphates and sulphates, if it is to produce food; and, however well supplied with alkalies and silica, if phosphates and sulphates be wanting, it can only produce leaves and stems to a certain point, but no seeds or esculent roots, &c. containing albuminous compounds. No supply of ammonia can produce albuminous compounds, if phosphates and sulphates be not also supplied to enable the plants to employ the ammonia in the formation of the albuminous bodies.

When, by an extraordinary supply of any one mineral ingredient, or of ammonia, a large crop has been obtained, it is not to be expected that a repetition of the same individual manure next year will produce the same effect. It must be remembered, that the unusual crop has exhausted the soil probably of all the other mineral ingredients, and that they also must be restored before a second crop can be obtained. An analysis of the ashes of the crop will tell us what to restore.

The salt most essential to the growth of the potato is the double phosphate of ammonia and magnesia; that chiefly required for hay is phosphate of lime; while for almost all plants potash and ammonia are highly beneficial, and sulphates and phosphates are indispensable.

From the principles above mentioned we may deduce a few valuable conclusions in regard to the chemistry of agriculture. First, By examining the ashes of a thriving plant, we discover the mineral ingredients which must exist in a soil to render it fertile for that plant. Secondly, By examining a soil, we can say at once whether it is fertile in regard to any plants the ashes of which have been examined. Thirdly, When we know the defects of a soil, the deficient matters may be easily obtained and added to it, unmixed with such as are not

required. Fourthly, The straw, leaves, &c. of any plant must be the best manure for that plant, since every vegetable extracts from the soil such matters alone as are essential to its growth. This important principle has been amply verified by the success attending the use of wheat-straw or its ashes as manure for wheat, and of the clippings of the vine as manure for the vineyard. Where these are used no other manure is required. Fifthly, In the rotation of crops, those should be made to follow which require different minerals; or a crop which extracts comparatively little mineral matter, such as peas, should come after one which exhausts the soil of its phosphates and potash.

Of the chemical manures now so much used, *bone-dust* supplies the phosphates which have been extracted by successive crops of grass and corn, the whole of the bones of the cattle fed on these crops having been derived from the soil; its gelatine also yields ammonia by putrefaction. *Guano* acts as a source of ammonia, containing much oxalate and urate of ammonia; but its chief value depends undoubtedly on the phosphates which it contains, and which are derived from the fish which served as food to the sea-fowl, whose excrements constitute guano. These fish fed on others, or on animalcules, which in their turn fed on sea-plants. The sea-plants obtained their phosphates from the sea, which contains phosphates, and into which we have always been in the habit of sending the accumulated excreta, solid and liquid, of our cities. As the inhabitants of those cities fed on grain and meat, it is obvious that we only recover in guano a part of what we had thrown away. *Night-soil* and *urine*, especially the latter, are most valuable for the ammonia they yield, and still more for phosphates and potash, but are very much neglected in this country, although their importance is fully appreciated in Belgium and China. *Bran* is a very valuable manure, especially for potatoes, as it contains much of the ammoniaco-magnesian phosphate.

Nitrate of soda probably acts by its alkali, replacing potash, but it is possible that its acid may also yield nitrogen to plants, although we possess at present no evidence of this, and indeed no evidence that plants can derive their nitrogen from any other source than from ammonia.

It must never be forgotten, that if plants are supplied, either from the soil or in the manure, with the indispensable mineral salts, namely, the alkalies, silica, phosphates, sulphates, lime, and magnesia, they will supply themselves with ammonia from the atmosphere. The effect of supplying ammonia in the manure is simply to enable the plants to complete their growth in a shorter period, a matter of the utmost im-

portance in our climate, but of much less consequence in tropical and southern climates, where the summer is so much longer.

Such is a brief sketch of the general laws of vegetation as at present known, in so far as they are connected with chemistry. Of the changes in the juices of vegetables, by which the numerous products of the vegetable kingdom are formed, we know nothing. The juices of plants contain ammonia and sugar, gum or starch; all the elements are therefore present from which the azotized compounds, albumen, fibrine, and caseine, in other words, the albuminous compounds, may be formed, and it appears that vegetables alone can produce these. Thus, the final products of vegetation form the food of animals; the albuminous bodies serving for nutrition properly so called, and the starch, gum, sugar, and oil serving for the support of respiration.

The life of animals is distinguished chemically from that of vegetables, by the circumstance, that in the former oxygen is constantly absorbed and replaced by carbonic acid, while in the latter carbonic acid is absorbed, its carbon retained, and its oxygen given out. Consciousness and the power of locomotion are peculiar to animals.

In animals two processes are constantly carried on: that of respiration, by which the animal heat is kept up; and that of nutrition, by which the matter consumed in the vital functions and expelled from the body is restored.

Respiration is essentially a combustion of carbon and hydrogen, which in combining with oxygen are converted into carbonic acid and water, and at the same time furnish the animal heat. Liebig calculates that the amount of carbon daily burned in the body of an adult man is about fourteen ounces, and that the heat given out is fully sufficient to keep up the temperature of the body, and to account for the evaporation of all the gaseous matter and water expelled from the lungs.

This carbon is derived in the first place from the tissues of the body, which undergo a constant waste, but ultimately from the food.

In the carnivora, whose food is almost entirely composed of compounds such as albumen, &c., one part is devoted to supply the waste of the tissues, while another portion, or a corresponding amount of previously existing tissue, is decomposed so as to yield the carbon required for respiration. As the tissues can only be decomposed by the exercise of the vital functions, this is the reason why, in the carnivora, an enormous amount of muscular motion is required to furnish the necessary supply of carbon.

On the other hand, the food of the herbivora contains but little of the albuminous compounds, only sufficient to restore the waste of the tissues; while the carbon required for respiration is supplied by the

starch, gum, sugar, oil, &c. which form the great mass of their food, and no such amount of muscular motion is required in them as in the *carnivora*.

It is in the form of bile chiefly that the carbon undergoes combustion. Hitherto, the true function of the bile has been disputed; and by most authors that fluid has been considered as an excretion, intended to be expelled from the body in the *fæces*. But Liebig has shewn that only a small fraction of the whole amount of bile can be detected in any shape in the *fæces*, and that the bile unquestionably is reabsorbed in the intestinal canal and re-enters the circulation, where it soon disappears; and as the proportion of carbon in the bile is very large, although not sufficient to account for all the carbonic acid given out, there is no reason to doubt that it is gradually consumed by the oxygen of the arterial blood, and converted into carbonic acid and water, which escape by the lungs and skin. The recent discovery by Liebig of the presence of a large quantity of lactic acid in the juice of flesh, renders it probable that the bile is resolved into lactic acid and other products before it is finally consumed.

To return to the subject of the animal heat: the food that is required, and hence the appetite, must be proportional to the amount of carbon required to supply the animal heat. Now, in hot climates, where the external cooling is less, less heat is required, the appetite is much more feeble, and the usual food, consisting of fruits and vegetables, contains a far smaller amount of carbon than in cold climates, where the appetite is keen, and the food highly carbonized, such as flesh or even blubber. For the same reasons, warm clothing, by diminishing the loss of heat by external cooling, blunts the appetite; and those who remove from a cold to a warm climate always find that their appetite fails. This is a warning from nature to diminish the amount of food taken; and if it were attended to, and the common but absurd practice of stimulating the appetite by ardent liquors and hot spices abandoned, Europeans might enjoy as good health in the East or West Indies as at home. It is obvious, that, even in Europe, more food is required in winter than in summer. (*Animal Chemistry*, 23.)

In endeavouring to explain the formation of the bile, it is obviously of no moment whether we derive it from the albumen, fibrine, &c. of the food, or those of the tissues, their composition being identical. In his "*Animal Chemistry*," Liebig endeavoured to shew, taking the then admitted formulæ for bile and for blood, that the latter fluid, with the addition of a little water and oxygen, might be resolved into choleic acid and urate of ammonia, that is, into bile and urine. The

recent discovery of the presence of sulphur in choleic acid renders necessary a revision of all these formulæ, and that of blood can only be, at present, an approximation; but it cannot be doubted that some such changes must occur, and that they take place according to strictly chemical laws. The idea of Liebig, therefore, is of great value in animal chemistry.

Supposing it to be well founded, the tissues which are consumed are resolved first into bile and urate of ammonia. The former is secreted from the liver, reabsorbed and burned, as before stated. The latter, in serpents and birds, is expelled unchanged; but in man and quadrupeds, in whom the amount of oxygen inspired is much greater, it also is oxidized, yielding finally carbonic acid, ammonia, and urea.

Should the supply of oxygen in the human subject be insufficient to act on the urate of ammonia, then the uric acid is deposited as gravel or calculus; if the supply of oxygen be somewhat greater, but still deficient, oxalic acid is the result, and mulberry calculus occurs; but, if much exercise be taken and abundance of oxygen supplied, the oxidation of the uric acid is completed, and nothing is left but urea or carbonate of ammonia.

This explains the true cause of uric acid and mulberry calculus to be a deficiency of oxygen; it also explains why uric acid calculus is followed by mulberry calculus in those who remove from the town to the country, where more exercise is taken; and from these considerations we may see how valuable are the results which will flow from a thorough investigation of all departments of animal chemistry.

The urine of the herbivora differs from that of man, in containing, besides urea, much hippuric acid when they are at rest or stall-fed, and benzoic acid when they are in full exercise, and when consequently more oxygen is supplied.

The bile of the herbivora is much more abundant than that of the carnivora, an ox secreting, according to Burdach, 37 lb. of bile daily. As the waste of matter in the herbivora is but limited, it is obvious that it cannot supply all the bile, and consequently a great part of it must be derived from the starch and other non-azotized constituents of their food, which lose oxygen, and enter into combination with some azotized product of the decomposition of the tissues.

For the reasons formerly mentioned, we omit here Liebig's equations explanatory of the production of bile from albuminous compounds and starch, since, until new analyses shall have been made, they would mislead the student.

We have thus seen how the carbon in the form of choleic acid or bile may be obtained in a state most favourable for its oxidation or com-

bustion. But, if the supply of oxygen be deficient, the choleic acid may by a partial oxidation yield hippuric and lithofellic acids, just as we have seen that uric acid, partially oxidized, yields oxalic acid. Thus, one species of biliary calculus, identical with the bezoar stones found in the herbivora, may have an origin similar to that of the mulberry calculus, both arising from a deficient supply of oxygen. (Liebig.)

Soda is necessary to the formation of bile, and is supplied in the form of common salt: where the supply of soda is defective, the metamorphosis of albuminous compounds can yield only fat and urea. Now, it is worthy of observation, that, if we wish to fatten an animal, we must carefully avoid giving much salt in its food. (Liebig.)

In the urine of the carnivora we find soda in moderate quantity, combined with sulphuric and phosphoric acids. This soda was contained in their food, and, after contributing to form the bile, has been excreted by the kidneys. But it is never sufficient to neutralize the acids produced, and consequently we find much ammonia along with it, while the urine is acid.

But in the urine of the herbivora soda is present in far larger quantity, and combined with carbonic, hippuric, or benzoic acid. This shews that the herbivora require a far greater amount of soda than is contained in the amount of blood-constituents daily consumed, which in them is small; and this soda is obtained from their food, and employed in producing their abundant bile.

The plants on which the herbivora feed cannot grow in a soil destitute of alkalies; but these alkalies are not less necessary for the support of the animals than of the plants. The soda is found in the blood and bile; and the potash is now known to exist in large quantity in the juice of flesh, and to be absolutely essential to the production of caseine, that is, the secretion of milk. In like manner the phosphate of lime, which is essential to the growth of grasses, is equally essential to the production of bone in the animals which feed on these plants. It is impossible not to be penetrated with admiration of the wisdom which is shewn in these beautiful arrangements.

Let us now consider the changes which the food undergoes in the process of digestion, and we shall observe this process in the carnivora, where it is most simple, as their food is identical in composition with their tissues.

When the food has entered the stomach, the gastric juice is poured out, and after a short time the whole is converted into a semifluid, homogeneous mass, the chyme. Many researches have been made to discover the solvent contained in the gastric juice, but in vain. It

contains no substance which has the property of dissolving fibrine, albumen, &c.; and we are compelled to adopt the opinion of Liebig, according to which the food is dissolved in consequence of a metamorphosis analogous to fermentation, by which a new arrangement of the particles is effected. As, in fermentation, the change is owing to the presence of a body in a state of decomposition, or motion which is propagated from the ferment to the sugar by contact; so, in digestion, the gastric juice contains a small quantity of a matter derived from the lining membrane of the stomach, which is in a state of progressive change, and the change or motion is propagated from this to the particles of the food under certain conditions, such as a certain temperature, and, as it now appears, the presence of a free acid, which is phosphoric or lactic acid, or both.

The phenomena of artificial digestion confirm this view. If the lining membrane of a stomach, perfectly clean and fresh, be infused in water feebly acidulated with hydrochloric acid, the liquid acquires no solvent action on albumen; but if the membrane be exposed to the air for some time, or be left in water for a while,—in short, if decomposition be allowed to commence,—then the infusion, if coagulated albumen or fibrine be placed in it, and the whole kept at the temperature of the body, by degrees effects a perfect solution or digestion.

Prout has shewn that the gastric juice, when distilled, yields free hydrochloric acid. This is derived from the common salt, the soda of which combines with the free phosphoric and lactic acids, and also with albumen and fibrine, while its acid, being set free, at length by its accumulation checks further change. Besides the gastric juice, the only other substance employed in digestion is the oxygen which is introduced into the stomach with the saliva, which from its viscosity encloses a large quantity of air. The chyme then leaves the stomach, and gradually passes into the state of chyle, which resembles blood, except in colour, being already alkaline, not acid like the chyme.

By means of the circulation oxygen is conveyed in the arterial blood to every part of the body. This oxygen, acting on the tissues destined to undergo change, produces a metamorphosis, by which new soluble compounds are formed. The tissues thus destroyed are replaced by the new matter derived from the food. Meantime, those of the products of metamorphosis which contain the principal part of the carbon are separated from the venous blood in the liver, and yield the bile; while the nitrogen accumulates, and is separated from the arterial blood in the kidneys, in the form of urea or uric acid.

The blood has another important function to perform, namely, to convey for excretion to the lungs the carbonic acid formed in the ex-

treme vessels or cells in all parts of the body. There is reason to believe that the globules of blood possess the property of absorbing oxygen in the lungs, when they become arterial, and then convey this oxygen to all parts. The globules then give up this oxygen to the particles of the tissues undergoing change, and in its stead carbonic acid is taken up, and the blood becomes venous. It is not known what chemical compound in blood absorbs and carries the oxygen, but it is by some conjectured to be a compound of iron, analogous to the protoxide. It is certain that iron is indispensable to the blood, and it is remarkable that sulphuretted hydrogen and hydrocyanic acid both instantly destroy the power of the blood to perform its functions; hence their terrible energy as poisons when inhaled. Now these compounds both act on protoxide, protochloride, and other analogous compounds of iron, immediately depriving them of their characteristic power of acting on oxygen.

With regard to the carbonic acid which is produced in all parts of the body in the continual metamorphosis of the tissues, this was long supposed to be absorbed and conveyed to the lungs by the carbonate of soda, which was thus for the time converted into bicarbonate, a salt which was supposed to give off in the lungs its excess of carbonic acid. But Enderlin has proved, at the suggestion of Liebig, that blood contains no carbonates whatever; and Liebig has more recently pointed out that the required properties exist in a still higher degree in the phosphate of soda, which does exist in the blood, and appears to be altogether indispensable to its existence. The experiments of Scheerer and those of Liebig have demonstrated that the common phosphate of soda (tribasic phosphate with 2 eq. of *fixed* base, $\text{PO}_5 + 2\text{NaO}$, HO) absorbs twice as much carbonic acid as carbonate of soda, and gives off the whole of it. No salt known is so well adapted for this function.

It is truly remarkable, that, while both phosphate of soda and phosphate of potash exist in the food, the former alone should occur in the blood; and this is especially wonderful when we consider that the juice of flesh, which is only separated from the blood by various thin membranes, permeable to liquids by endosmose and exosmose, contains much phosphate of potash and little or no phosphate of soda. It is evident that the vessels or cells must possess in their peculiar membranes a power of selection, or of allowing some salts to pass in one direction only and others in the opposite.

Another circumstance worthy of notice is, that, when earthy phosphates act on salts of potash, they always produce an acid salt, namely, tribasic phosphate of potash with 1 eq. of *fixed* base, $\text{PO}_5, \text{KO}, 2\text{HO}$;

while, when the same earthy phosphates and phosphate of potash act on salts of soda, they invariably produce an alkaline salt, namely, the phosphate of soda above mentioned with 2 eq. of fixed base, $\text{PO}_5, 2\text{NaO}, \text{HO}$.

Now the former of these, the acid phosphate of potash, the only phosphate that can be formed by an animal from food containing salts of potash without soda, such as inland plants, is the essential salt of the juice of flesh, but totally unfit for the formation of blood. The phosphate of soda in blood *cannot be replaced* as to its function by phosphate of potash. Here we see the beautiful discoveries of Graham concerning the phosphates, discoveries which at no distant period might have been regarded as possessing only a purely scientific interest, furnishing an explanation of some of the most important links in the chain of vital processes. There can be no doubt that the function of the acid salt, the phosphate of potash, in the juice of flesh, and apparently also in the gastric juice, is as important as that of phosphate of soda in the blood. Probably a part of that function is to ensure the constant acidity of these fluids, as phosphate of soda does the constant and essential alkalinity of the blood, on which, as we have seen, the power of absorbing and giving out carbonic acid, in other words, respiration, depends. And we see, too, that, if this be so, the phosphate of potash of the juice of flesh and of the gastric juice cannot be replaced, as far as its function is concerned, by phosphate of soda.

Another probable function of the substances which give acidity to the juice of flesh and alkalinity to the blood, is the production of electrical currents. It has been shewn by Matteucci that such currents exist in the body, and we can easily see how they may arise, when we observe two fluids, one acid the other alkaline, separated by a membrane, permeable to one or both, and the fluids in contact with muscle and with nervous matter. At the request of Liebig, (Researches on the Chemistry of Food, p. 104, note,) Buff constructed piles of discs of pasteboard steeped in blood, with slices of muscle and brain, which shewed a powerful current from the blood to the muscle.

Since no blood can be formed without soda, no animal could live if confined to such inland plants as contain only potash. It is well known, indeed, that animals in countries far inland, as Bavaria, are habitually supplied with common salt, either in substance or in the form of salt-springs. Of both they are instinctively fond. But, fortunately, salt is found in small quantity even in inland countries, in all soils and in all waters, and consequently in most plants. Were it altogether absent no blood could be formed, unless salt or soda were artificially supplied to every animal. All inland plants contain earthy

phosphates and phosphate of potash in variable proportion, often with mere traces of the compounds of sodium. When these phosphates act on common salt (chloride of sodium), there are formed chloride of potassium and the common alkaline phosphate of soda, which latter salt is absolutely indispensable to the formation of blood. The chloride of potassium is found in the juice of flesh.

It is truly a spectacle worthy of admiration to see the essential properties of two of the most important animal fluids, the blood and the juice of flesh, thus secured by the existence of a difference, at first sight altogether insignificant, between the relations of phosphoric acid to two alkalies, which so much resemble one another that they may be mutually replaced, each by the other, in a multitude of cases, nay, do actually replace each other in many plants. The reader will not fail to remark how emphatically these facts impress on us the necessity of attending carefully to the most minute characters of all the compounds which can be formed among the elements composing the organic kingdom, even when these characters appear at the time to have no conceivable relation to the vital processes.

Man being omnivorous, his mixed food contains all the constituents which are required for nutrition and respiration. The researches of Dr. R. D. Thomson have demonstrated that the most favourable proportion between the albuminous or azotized, and the saccharine or non-azotized constituents in the food of animals, is that of 1 part by weight of the former to 7 or 8 of the latter. This proportion exists naturally in the most nutritious food, such as grain, while in such food as potatoes the amount of albuminous matter is much too small. Hence, potatoes alone must be regarded as very inferior in nutritive power to wheat, oats, rye, or maize, equal weights being compared.

The art of cookery serves essentially to bring the food into a state better fitted for assimilation, and which mankind therefore instinctively prefer to the raw state; but, in ordinary cookery, many absurd and irrational practices prevail, for want of a truly scientific foundation for the art. In this, however, as in all similar cases, the long experience and observation of mankind has often led to that practice which is found on scientific principles to be the best.

When flesh is to be used as food, it is quite obvious, that, if any characteristic constituent be removed in preparing it, and not supplied from another source, it becomes so far unfit for producing flesh in the body. Hence it is altogether irrational to boil meat in a large quantity of water, and then, as is often done, to throw away the liquid, containing the greater part of the soluble constituents and salts, and to eat the boiled meat deprived of these valuable ingredients. The

meat, and the soup in which it was boiled, which ought not to be too bulky, should both be consumed, to convey into the system the whole of the original flesh.

There are, however, two different objects to be attained in boiling meat, and consequently two modes of boiling it. When the object is to make the meat palatable, and at the same time nutritious, the operation must be so performed that as little soluble matter as possible shall be extracted. To this end a mass of meat, of considerable size, is to be thrown into water when that liquid is boiling briskly, and the boiling kept up for a few minutes. So much cold water is now to be added as reduces the temperature to from 158° to 165° , and this temperature is to be kept up for some hours, or till the meat is thoroughly cooked in the centre.

The effect of the boiling water at first is to coagulate the albumen of the juice at the surface, and thus to form a crust which prevents any further exchange between the juice in the meat within the crust and the water without. The subsequent lower temperature is sufficient to coagulate the albumen and blood throughout, without hardening the fibrine, and the meat within thus acquires the taste, smell, and almost the aspect of well-roasted meat; it is juicy, tender, well-flavoured, and nutritious, while the soup is of no value. The deposition of the soft coagulated albumen around the fibrine protects the latter from the action of the boiling water, which would make it hard and horny, and is therefore one chief cause of the tenderness of well-boiled or roasted meat. In roasting, the heat ought to be gradually applied, and should never exceed 150° or 158° . Short of this the meat looks raw and bloody, because the colouring matter is not coagulated. Small pieces of flesh, as small birds, are protected from too strong a heat by a jacket of lard, which prevents even the surface from becoming tough, and keeps the meat juicy.

But if our object be to make good, strong, nutritious, and well-flavoured soup, we must adopt an opposite plan. The meat in thin slices is placed in cold water, which is very gradually raised to the boiling-point. Here, from the first, as no coagulation takes place till about 130° to 140° , a perfect exchange or mutual penetration of the juice and the water occurs, so that the water becomes charged with the soluble and sapid constituents of the flesh. Finally, coagulation takes place, the albumen rises to the surface and is removed as scum, and the fibrine at last becomes tough and hard. The meat, if now eaten without the soup, is insipid and innutritious, whereas the soup is well-flavoured, and contains almost all the matters necessary for digestion and nutrition.

It is generally believed that the strength of soup is proportioned to the amount of dissolved gelatine, as strong soup gelatinizes on cooling. But the amount of gelatine dissolved is very trifling, the whole amount of the excess of matter dissolved by hot water, after the juice has been removed by cold water, not exceeding one-fifth of the soluble substances as weighed after the albumen has been coagulated and removed, and of this fifth part only a portion is gelatine. 1000 parts of flesh yield to cold water 60 parts of soluble matter, of which about half is albumen, the other half kreatine, salts, &c. Hot water now dissolves only 6 parts, of which only part is gelatine, and on an average there are left 20 parts of fat and 164 parts of fibrine, membranes, vessels, &c. ; the rest, 750 parts, is water.

Fowl yields to cold water 80 parts of soluble matter from 1000, and of these 47 are albumen and 33 kreatine, lactates, phosphates, chlorides, &c.

Hence it follows that the best soup may be made by means of cold water, and consequently free from gelatine.

If 1 lb. of finely chopped meat be mixed with 1 lb. of cold water, and then slowly heated to boiling and boiled for a minute or two, hardly any gelatine is dissolved, and the liquid, strained to separate the coagulated albumen and the fibrine, forms about 1 lb. of the strongest and most aromatic soup that can be obtained from 1 lb. of flesh, such as cannot be made by boiling a mass of flesh for hours. When properly seasoned, and coloured by means of caramel, it is found to be preferable to all other soup.

When concentrated in the water-bath it becomes darker, and acquires a delicate flavour of roast meat. When dried up it constitutes the extract of meat or true portable soup, of which half an ounce, dissolved in 1 lb. of hot water, yields soup equal to the original. This is widely different from the portable soup of commerce, which consists chiefly of gelatine from bones.

Of the true extract, 80 parts per cent. are soluble in alcohol of 85 per cent., which dissolves only 4 or 5 per cent. of the commercial.

The true extract, according to Liebig, to whom we are indebted for these details, is an invaluable provision for ships, fortresses, &c. ; and, as long ago recommended by Prout and Parmentier, it is admirably adapted for the use of the wounded on the field, supplying them with strength to bear removal to the hospitals.

The salting of meat is detrimental to its nutritive qualities, because an exchange takes place between the salt and the juice. Meat rubbed with salt is soon floating in brine, and this brine contains and thus removes the greater part of the soluble and sapid constituents. The

extract of meat above mentioned is an admirable corrective of the bad effects of salt food.

The stock of cooks is nothing else than a true soup like that above recommended, which, being added to meat, improves its flavour, and increases its nutritive power. Its quality is judged of by the taste, because it depends on the proportion of sapid constituents. For the same reason, namely, the presence of lactates and free lactic acid, as well as chlorides of potassium and sodium, the addition of salt improves the flavour, as does also in a remarkable degree the moderate use of condiments containing lactic acid, such as sauer-kraut.

It has been already mentioned that vegetables alone possess the power of forming albuminous compounds, which they furnish to animals in the forms of albumen, fibrine, and caseine. In the animal body these substances are employed to yield the different tissues.

There is another constituent of the animal body, namely fat, the production of which deserves notice. It is not an organized tissue, but is formed and collected in the cellular tissue under certain circumstances. These are rest and confinement, that is, a deficiency of oxygen, and an abundance of food containing a considerable proportion of non-azotized matter, such as starch, sugar, &c. The artificial formation of butyric acid from sugar by contact with animal matter, demonstrates the possibility of the production of fat in this manner in the body. Carnivorous animals are never fat; and the herbivora only become so in confinement.

Now the chief source of fat is starch, or sugar, the composition of which is such, that, when deprived of oxygen, fat remains. If from starch, $C_{12}H_{10}O_{10}$, we take 9 at. oxygen, there remains $C_{12}H_{10}O$, which is one of the empirical formulæ for fat. Or if from starch we remove 1 at. carbonic acid, CO_2 , and 7 at. of oxygen, the remainder, $C_{11}H_{10}O$, represents the other empirical formula of fat. We have already seen that fat may be derived from albuminous matters when soda is deficient; and we may here add, that all the elements of food contain more oxygen than fat in proportion to the carbon. Thus, in albumen, fibrine, and caseine, for 120 eq. of carbon there are contained 36 eq. of oxygen; in starch, for 120 eq. carbon, 100 eq. oxygen; in sugar and gum, 110 eq. oxygen; in sugar of milk, 120 eq.; and in grape-sugar, 140 eq. oxygen; while in fat there are only 10 eq. of oxygen for 120 eq. of carbon.

It is obvious, therefore, that fat can only be formed by a process of deoxidation. But we have seen that it is produced where oxygen is deficient; and it appears, as Liebig has pointed out, that, when there is a deficient supply of oxygen, the production of fat, which is the con-

sequence of this deficiency, yields a supply of that element, and thus serves to keep up the animal heat and the vital functions, which would otherwise be arrested. This is another beautiful instance of contrivance, equally simple and wonderful.

That fat must be formed by the deoxidizing process above alluded to, is proved by the phenomena of the fattening of animals. A goose, tied up, and fed with farinaceous food, altogether destitute of fat, acquires in a short time an increase in weight of several pounds, the whole of which is fat. Again, the bee produces wax, a species of fat, from pure sugar.

With regard to the production of nervous matter, which animals alone can form, we see, from its composition, intermediate between that of albumen and fat, that it may be formed, either by depriving albuminous matter of some azotized product, or by adding to fat an azotized compound. Where it is formed we do not know, but it must be formed in the animal body; and Liebig has suggested that the power of the vegetable alkalies to affect the nervous system may be owing to their composition, which approaches nearer to that of nervous matter than any other compounds. These alkalies may promote or check the formation of nervous matter, and thus produce their peculiar effects.

In like manner, certain vegetable products analogous to the vegetable alkalies, such as caffeine (theine) and theobromine, may be supposed, according to Liebig, to promote the secretion of bile, their composition being related to that of some of the products of bile.

Now, it is surely very remarkable that the vegetables containing these compounds, tea, coffee, cocoa, guarana, and Paraguay tea, should be, one or other of them, used by almost all nations to yield a refreshing drink; and it is still more curious that the peculiar principle of tea, guarana, and Paraguay tea, should turn out to be identical with that of coffee, as recent researches have demonstrated.

We may suppose, with some degree of probability, that where the formation of bile, and consequently that of urine, which is connected with it, does not go on as it ought, the use of these beverages, by promoting the secretion of bile, may assist the process of respiration, promoting the animal heat, and at the same time contributing to the due performance of all the vital functions. At all events, neither the beneficial and refreshing effects of these articles of diet, nor their relation to bile and urine, can be overlooked; and the universal adoption of the practice of using tea, coffee, or chocolate, is a proof that men have discovered and obtained from different sources the means of producing the same effect.

The preceding observations are sufficient to shew that we may expect in progress of time to explain the action of all remedies on chemical principles. The true path has been opened up, and it only remains for experimenters to pursue it with energy and perseverance.

In the foregoing pages we have given only a very brief, imperfect, and condensed view of the principal facts recently ascertained in physiological chemistry, with the conclusions to which they naturally lead. Our space is too limited to permit us to do more than this ; and, indeed, to have entered more fully into this interesting subject would have been inconsistent with the character of an elementary work.

Enough has been done, however, to convince the reader that the practical applications of the modern organic chemistry are not less important than those which have been so happily made of the more early developed inorganic chemistry. We are only at the commencement of a period which promises to be richer in valuable discoveries, and in applications to the benefit of mankind than any which has preceded it.

Those who wish to become more intimately acquainted with the present state of physiological chemistry are referred to Liebig's "Agricultural Chemistry" and to his "Animal Chemistry," works which have led the way in these most important investigations, and the effect of which on the progress of discovery will long be felt ; also to the "Physiological Chemistry" of Mulder, now in course of publication ; to Liebig's latest work, his "Researches on the Chemistry of Food ;" and to the "Lectures on Physiological Chemistry" of Matteucci, of which a translation is now appearing in the "Lancet."

PART IV.

ANALYTICAL CHEMISTRY.

[*I am deeply indebted to MR. PARNELL for the Sections on Analysis, which he kindly undertook to furnish at my request; and would beg to refer the reader, who is desirous of more detailed instructions, to a very excellent treatise on Chemical Analysis, recently published by that gentleman; or to Dr. Will's Outlines of Analogies.—W. G.**]

THE subject of Chemical Analysis is so comprehensive, that to give more than a general outline of this branch of practical chemistry, would be inconsistent with the plan of these Elements.

The few following observations are thrown into four sections: the first of which comprises general instructions concerning the manipulations necessary in analytical processes; the second contains a few directions for the performance of qualitative analysis; the third, for the quantitative estimation of the most common constituents of minerals; and the fourth, for the analysis of mineral waters.

An analysis may have for its object the estimation of the weights of either the ultimate or proximate constituents of a substance, that is, of the ultimate elements of which a body is composed, without reference to the manner in which those elements are arranged, or of the proximate compounds which form, by their immediate union, the substance in question. In organic analysis, the proximate constituents are the substances generally sought; and the elementary composition of these being already known, the ultimate elements of which the substance analyzed is composed are also ascertained.

Before the composition of a substance can be determined quantitatively, it is necessary to have the nature or quality of the constituents accurately determined; and thus a chemical analysis is resolved into two distinct examinations: first, for the nature of the constituents, which is called the *qualitative analysis*; and, second, for the respective weights of these constituents, which is the *quantitative analysis*. As an example, it might be ascertained merely that crystallized sulphate of magnesia is composed of magnesia, sulphuric acid, and water; or that the salt mentioned contains, in 100 parts, 16·7 of magnesia, 32·4 of sulphuric acid, and 50·9 of water.

* London: Taylor and Walton.

SECTION I.

MANIPULATIONS IN ANALYTICAL PROCESSES.

In qualitative analysis the presence of any particular ingredient in the substance under examination is generally ascertained by mixing a test-liquid with a solution of the substance operated on, and observing, by the occurrence or non-occurrence of a precipitate, whether the suspected substance is present or not. If the test-liquid which is added produces no precipitate with any other substance whatever than that sought for, this simple operation is conclusive as to the presence or absence of the suspected body: but if, on the other hand, a test-liquid can produce a precipitate with more than a single substance, it becomes necessary to apply other tests before positive evidence of the presence of a particular substance is obtained. For example, if a neutral solution is to be tested for sulphuric acid, a solution of nitrate of baryta or chloride of barium is added to the liquid: the absence of a precipitate in that case is conclusive as to the absence of sulphuric acid. But if a precipitate occurs, it might be produced in a neutral solution by other acids besides sulphuric; namely, boracic, phosphoric, hydrofluoric, arsenic, and a few others. The precipitates, however, which are produced by these acids in solutions of salts of barytes are soluble in nitric or hydrochloric acid, while sulphate of barytes is not. If either nitric or hydrochloric acid, therefore, is added to the mixture with the barytic salt containing the precipitate, the solubility or insolubility of the latter shews whether or not it contains sulphuric acid.

Fig. 20.



The mixture of the solution of the substance to be analyzed with the test-liquid may be made either in a conical wine-glass or in a test-tube. The wine-glass should be provided with a spout for the convenience of pouring liquids into a tube or flask, with the view of applying heat, an operation frequently necessary. Instead of a wine-glass, a test-tube (*fig. 20*) is frequently employed, which possesses the advantage of allowing heat to be applied without transferring the liquid to another vessel. A convenient size for ordinary use is four inches in length, by

two-thirds of an inch in diameter.

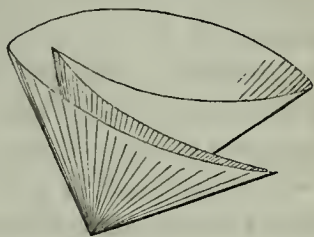
When it is necessary to examine the action of a test-liquid on a precipitate obtained in the course of testing, that may sometimes be

done in the same glass or tube; but often it is requisite to separate the precipitate wholly from the solution, which is accomplished by *filtration*. The process of filtering is one on which the success of analyses, both qualitative and quantitative, but especially of the latter, materially depends.

Filtration is effected by means of a paper filter, formed by doubling twice a circular piece of filtering paper, so as to form a quadrant, and then opening one of the folds, as shewn in *fig. 21*. The filter is supported in a glass funnel, which is itself held in any convenient manner; a vessel being placed below the funnel to receive the filtered liquid. Before pouring the turbid liquid on it, the filter should be wetted with a few drops of distilled water, which has the effect of swelling the fibres of the paper, without which precaution the liquid would not at first pass through clear. As the loss of a single drop of the liquid might, in quantitative analysis, render the operation worthless, its transference to a filter must always be directed by a glass rod, applied to the lip of the containing vessel, and held nearly perpendicular, with its extremity very near, but not touching the filter (see *fig. 22*).

In quantitative analysis, the substance whose weight is to be determined is generally separated from the solution in which it is contained by precipitation in a solid form, which is capable of being weighed, and which contains a known proportion of the substance to be estimated. If, for example, the amount of copper contained in a solution is required, that metal is precipitated in the state of oxide by caustic potassa: when washed and perfectly dried, the precipitated oxide may be weighed; and as it is known to contain, in 100 parts, 79.83 parts of copper, the quantity of the metal contained in any amount of the oxide is readily learned by calculation.

The whole of the precipitate having been collected on the filter, as already described, it is washed with pure distilled water until every trace of the original liquid is removed, and then dried on the filter in

Fig. 21.*Fig. 22.*

a hot drying-stove at any temperature below 212° . When dry, if the substance is not decomposed by being heated to redness, it is held, being still on the filter, immediately over a porcelain or platinum crucible, the weight of which when empty is already known; the paper is set on fire, and the precipitate is allowed to fall into the crucible, together with the ash of the filter. The crucible should be placed over a piece of highly-glazed coloured paper, to retain any particles of the precipitate which may fall on it, and which are afterwards carefully put into the crucible. After the matter has been heated to redness, if the filter has been completely burned, the crucible with its contents is weighed, and the weight of the empty crucible is deducted from the entire weight. The ash of the filter, also, the average weight of which is determined by previous experiments, must be subtracted from the weight of the heated mass.

In those cases in which the precipitate to be weighed cannot be heated to redness without suffering decomposition, the filter in which it is to be collected should be carefully dried, and introduced, folded, into a platinum crucible, which is then covered and weighed. The necessity of weighing the filter in a closed vessel arises from the circumstance, that dry paper rapidly absorbs hygrometric moisture from the air, which would prevent its weight being accurately determined if placed, open, on the pan of the balance. Having weighed the filter and crucible, the filtration may be conducted as usual; and, when the precipitate is washed and dried in the drying-stove, the filter containing it is folded, introduced into the same crucible, and weighed. After the first weighing the crucible should be uncovered and exposed to as high a temperature as paper will support without charring, to discover if any loss in weight is experienced through the escape of water, from the mass not having been previously rendered perfectly dry. The weight of the empty crucible and filter, deducted from the entire weight, gives that of the precipitate.

Such is an outline of the methods usually followed in determining the weights of the ingredients of compound bodies. There are, however, many cases in which a different course is pursued, varying according to the nature of the substances and the degree of nicety required; but a description of these would improperly encroach on space which is devoted to another purpose.

SECTION II.

QUALITATIVE ANALYSIS.

In analytical processes the first object is to obtain the substance in a proper state of solution. If soluble in water, that fluid is preferred to every other menstruum; but, if not, an acid or any convenient solvent may be employed. In many instances, however, the substance to be analyzed resists the action even of acids, and in that case the following method is adopted:—The compound is first crushed by means of a hammer or steel mortar, and is afterwards reduced to an impalpable powder in a mortar of agate; it is then intimately mixed with three, four, or more times its weight of potassa, soda, baryta, or their carbonates; and, lastly, the mixture is exposed in a crucible of silver or platinum to a strong heat. During the operation, the alkali combines with one or more of the constituents of the mineral; and, consequently, its elements being disunited, it no longer resists the action of the acids.

The following brief observations on qualitative analysis have reference to the discovery of the constituents of a salt soluble in water, and which consists of a single acid and a single base, to ascertain which two distinct operations are in general necessary.

The bases, for the detection of which means are pointed out, are the following:—

- | | |
|----------------------------|---------------|
| 1. Oxide of Copper. | 10. Alumina. |
| 2. Oxide of Lead. | 11. Magnesia. |
| 3. Protoxide of Tin. | 12. Lime. |
| 4. Peroxide of Tin. | 13. Strontia. |
| 5. Peroxide of Iron. | 14. Baryta. |
| 6. Protoxide of Iron. | 15. Ammonia. |
| 7. Oxide of Chromium. | 16. Potassa. |
| 8. Protoxide of Manganese. | 17. Soda. |
| 9. Oxide of Zinc. | |

1. A portion of the solution of the substance under examination is strongly acidified by a mineral acid, and saturated with sulphuretted hydrogen gas, or else is mixed with water strongly impregnated with that gas.

If a black or brownish black precipitate is formed, the base is one of the first three in the list, namely, oxide of copper, oxide of lead, or protoxide of tin. To distinguish these three bases, add to other portions of the original solution the three following special tests:—

(a.)—Ammonia; which gives an intense blue liquid with solutions of *copper*.

- (b.)—Iodide of potassium ; which produces a fine yellow precipitate of iodide in solutions of *lead*.
- (c.)—Bichloride of mercury ; which gives with solutions of *proto-salts of tin*, first a white precipitate of calomel, and afterwards a black precipitate of metallic mercury. The solution supposed to contain a proto-salt of tin should be added gradually to the bichloride of mercury, and not in the reverse order, so that the bichloride is at first in large excess.

If a yellow or milky-white precipitate is produced by sulphuretted hydrogen, the base may be either peroxide of tin or peroxide of iron : the precipitate in the former case being the bisulphuret of tin ; and in the latter, free sulphur, proceeding from the decomposition of sulphuretted hydrogen by peroxide of iron, the latter being at the same time reduced to the state of protoxide.

- (a.)—If the base is *peroxide of iron*, yellow prussiate of potash gives, with the original solution, a deep blue precipitate of Prussian blue.
- (b.)—If the base is peroxide of tin, caustic potassa produces in the original solution a white precipitate of peroxide of tin, which may redissolve in an excess of the alkali, and which, if collected and ignited strongly, becomes insoluble in acids.
2. If sulphuretted hydrogen produces no precipitate in the acid solution of the substance, render another portion of the solution alkaline by ammonia, and then add an excess of hydrosulphuret of ammonia.

- (a.)—The formation of a black precipitate by hydrosulphuret of ammonia indicates the presence of *protoxide of iron*, in which case the original solution gives a deep blue precipitate with the red prussiate of potash.
- (b.)—If hydrosulphuret of ammonia gives a dull green precipitate, the base is *oxide of chromium*. If the precipitate is collected and fused with a bead of microcosmic salt before the blowpipe, the bead is found to be red while hot, but green when cold.
- (c.)—If hydrosulphuret of ammonia gives a flesh-colour precipitate, the base is *manganese* ; in which case a solution of chloride of lime produces in the original solution a dark brown precipitate of hydrated peroxide of manganese.
- (d.)—If hydrosulphuret of ammonia gives a white precipitate, the base may be either *oxide of zinc* or *alumina*. These substances may be distinguished by ammonia, which added to the original solution produces a white precipitate in both

cases; but oxide of zinc is soluble in excess of the alkali, while alumina is not.

3. If neither sulphuretted hydrogen nor hydrosulphuret of ammonia produces a precipitate, add a solution of carbonate of soda to another portion of the solution. The occurrence of a precipitate shews that the base is either magnesia, lime, strontia, or baryta, to distinguish which the original solution is tested in the following manner:—

(a.)—If a solution of oxalate of ammonia gives no precipitate, the base is *magnesia*.

(b.)—If oxalate of ammonia gives a precipitate, but dilute sulphate of soda does not, the base is *lime*.

(c.)—If dilute sulphate of soda gives a precipitate, the base is either *baryta* or *strontia*. These earths may be distinguished by a solution of hyposulphite of soda, which precipitates baryta, but not strontia.

4. If carbonate of soda gives no precipitate, the base is then one of the three alkalis, ammonia, potassa, or soda.

(a.)—If *ammonia*, the odour of that alkali is recognized on adding caustic potassa.

(b.)—A strong solution of tartaric acid gives a white crystalline precipitate of bitartrate of potassa if the base is *potassa*.

(c.)—Salts of *soda* are best distinguished by the yellow colour which they communicate to the flame of alcohol.

The base of the salt having been discovered, the examination for the acid may then be performed. The acids for the detection of which instructions are given are the following:—

- | | |
|--------------------|-------------------|
| 1. Carbonic. | 8. Boracic. |
| 2. Sulphurous. | 9. Hydrofluoric. |
| 3. Hydrosulphuric. | 10. Iodic. |
| 4. Hydriodic. | 11. Hydrochloric. |
| 5. Sulphuric. | 12. Nitric. |
| 6. Phosphoric. | 13. Chloric. |
| 7. Arsenic. | |

1. To the saturated solution of the salt in water, if soluble, or to the dry salt, if insoluble, dilute sulphuric acid is applied. The effervescence of a gas may proceed from carbonic, sulphurous, or hydrosulphuric acid. A developement of free iodine may proceed from hydriodic acid.

Carbonic.—The gas evolved is inodorous, and, when passed through lime-water, causes a white precipitate, which dissolves on transmitting an excess of the gas.

Sulphurous.—The evolved gas has the pungent smell of burning sulphur.

Hydrosulphuric.—The gas has a foetid odour, and the solution of the substance produces a black precipitate in salts of lead.

Hydriodic.—To detect hydriodic acid (iodides), mix the solution of the substance with a little solution of starch, and allow chlorine gas to fall on the surface of the liquid: the blue iodide of starch is formed.

2. If sulphuric acid produces neither effervescence nor developement of free iodine, add a solution of nitrate of baryta to the neutral solution of the substance. The acids which may be precipitated thereby are the following:—

Sulphuric.—The precipitate is insoluble in pure hydrochloric acid.

Hydrofluoric.—The powdered substance, gently heated with oil of vitriol in a platinum crucible, evolves a vapour which corrodes glass.

Arsenic (Arsenious).—Sulphuretted hydrogen gas, passed through the solution of the substance, strongly acidified by hydrochloric acid, gives a yellow precipitate of sulphuret of arsenic. This precipitate being dried, mixed with black flux, and heated to redness in a glass tube, gives a sublimate of metallic arsenic.

Phosphoric.—Nitrate of silver gives, with the neutral solution of the substance, a yellow precipitate of phosphate of silver, soluble in nitric acid.

Boracic.—If the dry substance is moistened with oil of vitriol, and then alcohol added, the latter burns with a green flame.

Iodic.—Sulphurous acid developes free iodine in the original solution; the presence of iodine may then be ascertained by its action on starch.

3. If dilute sulphuric acid produces no effervescence, and nitrate of baryta no precipitate, the acid may be hydrochloric, hydriodic, nitric, or chloric; in which case add nitrate of silver to the solution of the substance.

(a.)—If a yellow precipitate is formed, the acid may be *hydriodic*, which is known by the insolubility of the precipitate (iodide of silver) in solution of ammonia.

(b.)—If a white curdy precipitate is formed by nitrate of silver, the acid is *hydrochloric*; in which case the precipitate (chloride of silver) is readily dissolved by ammonia.

4. If nitrate of silver produces no precipitate, the acid is either *nitric* or *chloric*. To detect nitric acid, add the dry substance under examination to a mixture of protosulphate of iron and oil of vitriol; immediately, or on heating, a brown colour is developed, owing to nitric oxide.

To detect chloric acid, add oil of vitriol to the dry salt: peroxide of chlorine is evolved, and the liquid bleaches vegetable colours.

QUALITATIVE ANALYSIS OF GASES.

Table exhibiting the distinctive properties of oxygen, nitrogen, protoxide of nitrogen, deutoxide of nitrogen, hydrogen, carbonic oxide, and carbonic acid.

(From Graham's "Elements of Chemistry.")

GASES.

Soluble in Water	{ Carbonic Acid Protoxide of Nitrogen	{ Solution disturbs Lime-water. Does not.
Support combustion	{ Oxygen Protoxide of Nitrogen.	
Combustible	{ Carbonic Oxide Hydrogen	{ Product of combustion disturbs Lime-water. Does not.
Extinguish combustion	{ Deutoxide of Nitrogen Nitrogen	{ Forms brown fumes with Oxygen. Does not.

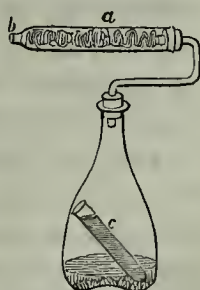
SECTION III.

QUANTITATIVE ANALYSIS.

The following observations on Quantitative analysis relate chiefly to those earthy minerals with which the beginner usually commences his labours, the most common constituents of which are silica, alumina, iron, manganese, lime, magnesia, potassa, soda, and carbonic and sulphuric acids.

Analysis of Marble, or Carbonate of Lime.—The quantity of carbonic acid contained in marble and all other carbonates which are soluble in hydrochloric or sulphuric acid in the cold may be determined by the following simple method:—A known weight of the powdered substance is introduced into a flask similar to that represented in *fig. 23*. The flask should be thin at the bottom to allow of the application of heat, and have the capacity of three or four ounces of water. It is fitted with a cork, which has a perforation to admit a small bent tube; and the latter is connected by means of another cork with a somewhat larger tube (*a*), containing fragments of dry chloride of calcium. The extremity *b* of this tube is drawn out so as to be capillary. The small tube (*c*) within the flask, sealed at one end, is intended to hold hydrochloric or sulphuric acid to decompose the carbonate, and is of such length that it

Fig. 23.



will not fall flat on the bottom of the flask, but rests against the side at an angle of about 45° with the bottom; so that, on inclining the flask, all the acid contained in this tube can be made to flow out. The apparatus being arranged, the weighed carbonate is introduced into the empty flask with about half an ounce of water; the small tube (*c*), containing sufficient hydrochloric or sulphuric acid to decompose the carbonate, is then introduced, taking care that no acid comes in contact with the carbonate, and the flask is closed by the cork attached to the chloride of calcium tube (*a*). The whole apparatus is now weighed; after which the flask is inclined, in order that a little of the acid in the tube *c* may flow out and come in contact with the carbonate, which is repeated until the latter is completely decomposed. As the evolved carbonic acid gas is dried in passing through the chloride of calcium tube (*a*), nothing else than this gas escapes, and the loss in weight of the apparatus at the close of the experiment is the weight of the carbonic acid required; but, as the flask is then full of carbonic acid gas, which is considerably heavier than air, it should not be weighed in its present state. To get rid of the remaining carbonic acid, the flask is very gently heated, so as to fill it with aqueous vapour, and thus drive out the gas, the steam itself not proceeding further than the chloride of calcium tube. On the condensation of the steam, air enters the flask, which, when cold, is in the same condition as it was when weighed before the decomposition of the carbonate, excepting only in the loss of carbonic acid.

Separation of Lime and Magnesia.—The more common kinds of carbonate of lime frequently contain traces of siliceous and aluminous earths, in consequence of which they are not completely dissolved in dilute hydrochloric acid. A very frequent source of impurity is carbonate of magnesia, which is often present in such quantity that it forms a peculiar compound called *Magnesian limestone*. The analysis of this substance, so far as respects carbonic acid, is the same as that of marble. The separation of the two earths may be conveniently effected in the following manner:—The solution of the mineral in muriatic acid is evaporated to perfect dryness in a flat dish or *capsule* of porcelain; and, after redissolving the residuum in a moderate quantity of distilled water, a solution of oxalate of ammonia is added as long as a precipitate ensues. The oxalate of lime is then allowed to subside, collected on a filter, dried, and decomposed by a red heat; and after moistening the resulting carbonate with a strong solution of carbonate of ammonia, in order to supply any particles of quicklime with carbonic acid, it should be dried, heated to low redness, and regarded as pure carbonate of lime. To the filtered liquid, containing

the magnesia, a mixture of pure ammonia and phosphate of soda is added, when the magnesia is precipitated in the form of the ammoniacophosphate. Of this precipitate, heated to redness, 100 parts, according to Stromeier, correspond to 37 of pure magnesia.

The precipitation of magnesia by means of phosphoric acid and ammonia, though extremely accurate when properly performed, requires several precautions. The liquid should be cold, and either neutral or alkaline. The precipitate is dissolved with great ease by most of the acids; and Stromeier has remarked, that some of it is held in solution by carbonic acid, whether free or in union with an alkali. The absence of carbonic acid should therefore always be ensured, prior to the precipitation, by heating the solution to 212° , acidulating at the same time by hydrochloric acid, should an alkaline carbonate be present. Berzelius has also observed, that, in washing the ammoniacomagnesian phosphate on a filter, a portion of the salt is dissolved as soon as the saline matter of the solution is nearly all removed; that is to say, it is dissolved by pure water. But Fresenius has shewn that it is quite insoluble in ammonia, so that it is only necessary to complete the washing with water containing a small proportion of ammonia.

Earthy Sulphates.—The most abundant of the earthy sulphates is that of lime, the analysis of which is easily effected. By boiling it for fifteen or twenty minutes with a solution of twice its weight of carbonate of soda, double decomposition ensues; and the carbonate of lime, after being collected on a filter and washed with hot water, is heated to low redness and weighed.

Of the dry carbonate, fifty parts correspond to twenty-eight of lime. The alkaline solution is acidulated with hydrochloric acid, and the sulphuric acid thrown down by chloride of barium. From the sulphate of baryta, collected and dried at a red heat, the quantity of acid may easily be estimated.

The method of analyzing the sulphates of strontia and baryta is somewhat different. As these salts are difficult of decomposition in the moist way, the following process is adopted:—The sulphate, in fine powder, is mixed with three times its weight of carbonate of soda, and the mixture is heated to redness in a platinum crucible for the space of an hour. The ignited mass is then digested in hot water, and the insoluble earthy carbonate collected on a filter. The other parts of the process are the same as the foregoing.

Mode of analyzing Compounds of Silica, Alumina, and Iron.—Minerals thus constituted are decomposed by an alkaline carbonate, at a red heat, in the same manner as sulphate of baryta. The mixture

is afterwards digested in dilute hydrochloric acid, by which means all the ingredients of the mineral, if the decomposition is complete, are dissolved. The solution is next evaporated to dryness, the heat being carefully regulated towards the close of the process, in order to prevent any of the chloride of iron, the volatility of which is considerable, from being dissipated in vapour. By this operation, the silica, though previously held in solution by the acid, is entirely deprived of its solubility; so that, on digesting the dry mass in water acidulated with hydrochloric acid, the alumina and iron are taken up, and the silica is left in a state of purity. The siliceous earth, after subsiding, is collected on a filter, carefullyedulcorated, heated to redness, and weighed.

To the clear liquid, containing peroxide of iron and alumina, a solution of pure potash is added in moderate excess; so as not only to throw down those oxides, but to redissolve the alumina. The peroxide of iron is then collected on a filter,edulcorated carefully until the washings cease to have an alkaline reaction, and is well dried and ignited, as described at page 1330. This operation, however, should be done with care; since any adhering particles of paper, or other combustible matter, would bring the iron into the state of black oxide, a change which is known to have occurred by the iron being attracted by a magnet.

To procure the alumina, the liquid in which it is dissolved is boiled with hydrochlorate of ammonia, when chloride of potassium is formed, the volatile alkali is dissipated in vapour, and the alumina subsides. As soon as the solution is thus rendered neutral, the hydrous alumina is collected on a filter, dried by exposure to a white heat, and quickly weighed after removal from the fire.

Separation of Iron and Manganese.—A compound of these metals or their oxides may be dissolved in hydrochloric acid. If the iron is in a large proportion compared with the manganese, the following process may be adopted with advantage:—To the cold solution, considerably diluted with water, and acidulated with hydrochloric acid, carbonate of soda is gradually added, and the liquid is briskly stirred with a glass rod during the effervescence, in order that it may become highly charged with carbonic acid. By neutralizing the solution in this manner, it at length attains a point at which the peroxide of iron is entirely deposited, leaving the liquid colourless; while the manganese, by aid of the free carbonic acid, is kept in solution. The iron, after subsiding, is collected on a filter, and its quantity determined in the usual manner. The filtered liquor is then boiled with an excess of carbonate of soda; and the precipitated carbonate of manganese is collected, heated to full redness in an open crucible, by which it is con-

verted into the red oxide, and weighed. This method is one of some delicacy; but in skilful hands it affords a very accurate result. It may also be employed for separating iron from magnesia and lime, as well as from manganese.

But if the proportion of iron is small compared with that of manganese, the best mode of separating it is by succinate of ammonia or soda, prepared by neutralizing a solution of succinic acid with either of those alkalies. That this process should succeed, it is necessary that the iron be wholly in the state of peroxide, that the solution be exactly neutral, which may easily be insured by the cautious use of ammonia, and that the reddish-brown coloured succinate of peroxide of iron be washed with cold water. When the precipitate is washed clean, solution of ammonia should be poured on it to separate succinic acid, and the remaining peroxide of iron may be dried, cautiously ignited, and weighed. From the filtered liquid the manganese may be precipitated at a boiling temperature by carbonate of soda, and its quantity determined in the way above mentioned. The benzoate may be substituted for succinate of ammonia in the preceding process.

It may be stated as a general rule, that, whenever it is intended to precipitate iron by means of the alkalies, the succinates, or benzoates, it is essential that this metal be in the maximum of oxidation. It is easily brought into this state by digestion with a little nitric acid.

Separation of Manganese from Lime and Magnesia.—If the quantity of the former is proportionally small, it is precipitated as a sulphuret by hydrosulphuret of ammonia or sulphuret of potassium. The sulphuret is then dissolved in hydrochloric acid, and the manganese thrown down as usual by means of an alkali. But if the manganese is the chief ingredient, the best method is to precipitate it at once, together with the two earths, by a fixed alkaline carbonate at a boiling temperature. The precipitate, after being exposed to a low red heat and weighed, is put into cold water acidulated with a drop or two of nitric acid, when the lime and magnesia will be slowly dissolved with effervescence. Should a trace of the manganese be likewise taken up, it may easily be thrown down by hydrosulphuret of ammonia.

Stromeyer has recommended a very elegant and still better process for removing small quantities of manganese from lime and magnesia. The solution is acidulated with nitric or hydrochloric acid; bicarbonate of soda is gradually added in very slight excess, stirring after each addition, that the liquid may be charged with carbonic acid; and a solution of chlorine, or a current of the gas, is introduced. The protoxide of manganese is converted by the chlorine into the insoluble hydrated peroxide, while any traces of lime or magnesia, which might

otherwise fall, are retained in solution by means of carbonic acid. A solution of chloride of soda or lime is in fact our most delicate test for small quantities of manganese.

Mode of analyzing an earthy Mineral containing Silica, Iron, Alumina, Manganese, Lime, and Magnesia.—The mineral, reduced to fine powder, is ignited with three or four times its weight of carbonate of potassa or soda; the mass is taken up in dilute hydrochloric acid, and the silica separated in the way already described. To the solution, thus freed from silica and duly acidulated, carbonate of soda, or still better the bicarbonate, is gradually added, so as to charge the liquid with carbonic acid, as in the analysis of iron and manganese. In this manner the iron and alumina are alone precipitated, substances which may be separated from each other by means of pure potassa (page 1338). The manganese, lime, and magnesia may then be determined by the processes above described.

SECTION IV.

ANALYSIS OF MINERAL WATERS.

Rain water collected in clean vessels in the country, or freshly fallen snow when melted, affords the purest kind of water which can be procured without having recourse to distillation. The water obtained from these sources, however, is not absolutely pure, but contains a portion of carbonic acid, ammonia, and air, absorbed from the atmosphere. It is remarkable that this air is very rich in oxygen. That procured from snow water by boiling was found by Gay-Lussac and Humboldt to contain 34.8, and that from rain water 32 per cent. of oxygen gas. From the powerfully solvent properties of water, this fluid no sooner reaches the ground and percolates through the soil, than it dissolves some of the substances which it meets with in its passage. Under common circumstances it takes up so small a quantity of foreign matter, that its sensible properties are not materially affected, and in this state it gives rise to *spring, well, and river* water. Sometimes, on the contrary, it becomes so strongly impregnated with saline and other substances, that it acquires a peculiar flavour, and is thus rendered unfit for domestic uses. It is then known by the name of *mineral water*.

The composition of spring water is dependent on the nature of the soil through which it flows. If it has filtered through primitive strata, such as quartz rock, granite, and the like, it is in general very pure; but, if it meets with limestone or gypsum in its passage, a portion of these salts is dissolved, and communicates the property called *hardness*.

Hard water is characterized by decomposing soap, the lime of the former yielding insoluble compounds with the margaric and oleic acids of the latter. If this defect is owing to the presence of carbonate of lime, it is easily remedied by boiling, when free carbonic acid is expelled, and the insoluble carbonate of lime subsides. If sulphate of lime is present, the addition of a little carbonate of soda, by precipitating the lime, converts the hard into soft water. Besides these ingredients, the chlorides of calcium and sodium are frequently contained in spring water.

Spring water, in consequence of its saline impregnation, is frequently unfit for chemical purposes, and on these occasions distilled water is employed. Distillation may be performed on a small scale by means of a retort, in the body of which water is made to boil, while the condensed vapour is received in a glass flask, called a *recipient*, which is adapted to its beak or open extremity. This process is more conveniently conducted, however, by means of a still.

The different kinds of mineral water may be conveniently arranged for the purpose of description in the six divisions of acidulous, alkaline, chalybeate, sulphureous, saline, and siliceous springs.

1. Acidulous springs, of which those of Seltzer, Spa, Pyrmont, and Carlsbad are the most celebrated, commonly owe their acidity to the presence of free carbonic acid, in consequence of the escape of which they sparkle when poured from one vessel into another. Such carbonated waters communicate a red tint to litmus paper before, but not after being boiled, and the redness disappears on exposure to the air. Mixed with a sufficient quantity of lime-water, they become turbid from the deposition of carbonate of lime. They frequently contain the carbonates of lime, magnesia, and protoxide of iron, in consequence of the facility with which these salts are dissolved by water with carbonic acid.

2. Alkaline waters are such as contain a free or carbonated alkali, and consequently, either in their natural state, or when concentrated by evaporation, possess an alkaline reaction.

These springs are rare. The best instance I have met with is in water collected at the Furnas, St. Michael's, Azores, and sent to the Royal Society of Edinburgh by Lord Napier. These springs contain carbonate of soda and carbonic acid, and are almost entirely free from earthy substances. Of five different kinds of these waters which I examined, the greater part also contained protoxide of iron, hydrosulphuric acid, and chloride of sodium.

3. Chalybeate waters are characterized by a strong styptic inky taste, and by striking a black colour with the infusion of gall-nuts. The

iron is sometimes combined with hydrochloric or sulphuric acid ; but most frequently it is in the form of protocarbonate, held in solution by free carbonic acid. On exposure to the air, the protoxide is oxidized, and the hydrated peroxide subsides, causing the ochreous deposit so commonly observed in the vicinity of chalybeate springs.

To ascertain the quantity of iron contained in a mineral water, a known weight of it is concentrated by evaporation, and the iron is brought to the state of peroxide by means of nitric acid. The peroxide is then precipitated by ammonia and weighed ; and, if lime and magnesia are present, it may be separated from those earths by the process described in the last section.

Chalybeate waters are by no means uncommon ; but the most noted in Britain are those of Tunbridge, Cheltenham, and Brighton. The Bath water also contains a small quantity of iron.

4. Sulphureous waters, of which the springs of Aix-la-Chapelle, Harrowgate, and Moffat afford examples, contain hydrosulphuric acid, and are easily recognized by their odour, and by causing a brown precipitate with a salt of lead or silver. The gas is readily expelled by boiling, and its quantity may be roughly estimated by transmitting it through a solution of pure chloride of mercury, and weighing the sulphuret which is generated.

5. Those mineral springs are called saline, the character of which is derived from saline compounds. The salts which are most frequently contained in these waters are the sulphates and carbonates of lime, magnesia, and soda, and the chlorides of calcium, magnesium, and sodium. Potassa sometimes exists in them, and Berzelius has found lithia in the spring of Carlsbad. It has lately been discovered, that the presence of hydriodic acid in small quantity is not unfrequent. As examples of saline water, may be enumerated the springs of Epsom, Cheltenham, Bath, Bristol, Barèges, Buxton, Pitcaithly, and Toeplitz.

The first object in examining a saline spring is to determine the nature of its ingredients. Hydrochloric acid is detected by nitrate of oxide of silver, and sulphuric acid by chloride of barium ; and, if an alkaline carbonate be present, the precipitate occasioned by either of these tests will contain a carbonate of oxide of silver or baryta. The presence of lime and magnesia may be discovered, the former by oxalate of ammonia, and the latter by phosphate of ammonia. Potassa is known by the action of chloride of platinum. To detect soda, the water should be evaporated to dryness, the deliquescent salts removed by alcohol, and the matter insoluble in that menstruum taken up by a small quantity of water, and be allowed to crystallize by sponta-

neous evaporation. The salt of soda may then be recognized by the rich yellow colour which it communicates to flame. If the presence of hydriodic acid be suspected, the solution is brought to dryness, the soluble parts dissolved in two or three drachms of a cold solution of starch, and strong sulphuric acid or gaseous chlorine gradually added.

Having thus ascertained the nature of the saline ingredients, their quantity may be determined by evaporating a pint of water to dryness, heating to low redness, and weighing the residue. In order to make an exact analysis, a given quantity of the mineral water is concentrated in an evaporating basin as far as can be done without causing either precipitation or crystallization, and the residual liquid is divided into two equal parts. From one portion the sulphuric and carbonic acids are thrown down by nitrate of baryta, and, after collecting the precipitate on a filter, the hydrochloric acid is precipitated by nitrate of oxide of silver. The mixed sulphate and carbonate is exposed to a low red heat, and weighed; and the carbonate is then dissolved by dilute hydrochloric acid, and its quantity determined by weighing the sulphate. The chloride of silver, of which 143.42 parts correspond to 36.42 of hydrochloric acid, is fused in a platinum spoon or crucible, in order to render it quite free from moisture. To the other half of the concentrated mineral water, oxalate of ammonia is added for the purpose of precipitating the lime; and the magnesia is afterwards thrown down as the ammoniaco-phosphate, by means of ammonia and phosphoric acid. Having thus determined the weight of each of the fixed ingredients excepting the soda, the loss is of course the quantity of that alkali required.

The individual constituents of the water being known, it remains to determine the state in which they were originally combined. In a mineral water containing sulphuric and hydrochloric acids, lime, and soda, it is obvious that three cases are possible. The liquid may contain sulphate of lime and chloride of sodium, or chloride of calcium and sulphate of soda; or each acid may be distributed between both the bases. It was at one time supposed that the lime must be in combination with sulphuric acid, because the sulphate of that earth is left when the water is evaporated to dryness. This, however, by no means follows. In whatever state the lime may exist in the original spring, gypsum will be generated as soon as the concentration reaches that degree at which sulphate of lime cannot be held in solution. The late Dr. Murray, who treated this question with much sagacity; observes that some mineral waters, which contain the four principles above mentioned, possess higher medicinal virtues than can be justly ascribed to the pre-

sence of sulphate of lime. He advances the opinion, that alkaline bases are united in mineral waters with those acids with which they form the most soluble compounds, and that the insoluble salts obtained by evaporation are merely products. He therefore proposes to arrange the substances determined by analysis according to this supposition. (Edin. Phil. Trans. vii.) To this practice there is no objection; but it is probable that each acid is rather distributed between several bases, than combined exclusively with either.

Sea water may be regarded as one of the saline mineral waters. Its taste is disagreeably bitter and saline, and its fixed constituents amount to about 3 per cent. Its specific gravity varies from 1.0269 to 1.0285; and it freezes at about 28.5° F. A very complete analysis of the water of the English Channel was executed a few years ago by Dr. Schweitzer of Brighton, the results of which are subjoined:—

	Grains.
Water	964.74372
Chloride of Sodium	27.05948
Chloride of Potassium	0.76552
Chloride of Magnesium	3.66658
Bromide of Magnesium	0.02929
Sulphate of Magnesia	2.29578
Sulphate of Lime	1.40662
Carbonate of Lime	0.03301
	1000.00000

The water of the Dead Sea has a far stronger saline impregnation than sea water, containing one-fourth of its weight of solid matter. It has a peculiarly bitter, saline, and pungent taste, and its specific gravity is 1.211. According to the analysis of Marcet, 100 parts of it contain—muriate of magnesia 10.246, muriate of soda 10.36, muriate of lime 3.92, and sulphate of lime 0.054. In the river Jordan, which flows into the Dead Sea, Marcet discovered the same principles as in the lake itself.

Most spring waters, including sea water, contain traces of phosphates. In the case of sea water, this is proved by the existence of phosphates in marine plants, as well as in the animals which feed on them. The proportion is generally too small to be detected by the analysis of a small quantity. Dr. G. Wilson has lately observed that most or all springs, as well as sea water, contain likewise traces of fluorides.

6. Siliceous waters are very rare, and in those hitherto discovered the silica appears to have been dissolved by means of soda. The most remarkable of these are the boiling springs of the Geyser and Rykum in Iceland, a gallon of which, according to the analysis of Black, contains the following substances: (Edinburgh Philos. Trans. iii. 95:)—

	Geyser.	Rykum.
Soda	5.56	3.0
Alumina	2.80	0.29
Silica	31.50	21.83
Muriate of Soda	14.42	16.96
Sulphate of Soda	8.57	7.53

The hot springs of Pinnarkoon and Loorgootha in India are analogous to the foregoing. A gallon of the water yields about 24 grains of solid matter; and the saline contents, sent to Dr. Brewster by Mr. P. Breton, were found to consist of 21.5 per cent. of silica, 19 of chloride of sodium, 19 of sulphate of soda, 19 of carbonate of soda, pure soda 5, and 15.5 of water. (Edinburgh Journal of Science, No. xvii. p. 97.)

It is remarkable that nitrogen gas very generally occurs in hot springs. It was found by Longchamp in various hot springs of France, and a similar observation has been made by Dr. Daubeny. Its source is clearly referable to atmospheric air contained in water, which air has been deprived of its oxygen by chemical changes in the interior of the earth.

ANALYSIS OF ORGANIC SUBSTANCES.

As all organic substances are composed of the same few elements, the ultimate analysis of them consists of but a few operations. The proximate analysis of animal or vegetable products consists generally in the successive use of different solvents, such as water, alcohol, ether, acids, and alkalies. By means of these, we discover the presence of organic acids, sugar, gum, and other analogous compounds, soluble in water; of resins, alkaloids, and many other bodies, soluble in alcohol; of fats and fat oils, and the corresponding fatty or oily acids, besides many crystalline compounds, soluble in ether, and so on. No rules of universal application can be given; the chemist must be guided by the results of the action of such solvents in each particular case. Volatile oils are obtained by distillation with water; and colouring matters dissolve some in one, others in another, of the solvents above mentioned. In vegetables, the residue left after the action of all these menstruum is considered as lignine, or woody fibre, in many cases mixed with extractive or humus-like matters, formed by gradual oxidation.

When an organic compound, or proximate principle, has been obtained in a state of purity, its ultimate analysis may be made. The ordinary elements of such proximate principles are, carbon, hydrogen,

and oxygen, or their elements, with the addition of nitrogen. In a few cases sulphur also occurs.

Carbon and Hydrogen.—These elements are invariably determined in the forms of carbonic acid and water, and they are brought into those forms by burning the compound by means of oxide of copper or bichromate of lead, sometimes assisted by chlorate of potash, and used in large excess. The combustion is conducted in a long tube, closed at one end, and at the other communicating, first with a weighed tube filled with chloride of calcium, in which the water is arrested, and then with a weighed apparatus, devised by Liebig, containing strong aqua potassæ, in which the carbonic acid is absorbed. This is the principle on which all organic analyses are conducted, but for details the reader must be referred to the works written professedly on the subject, such as Rose's "Manual of Analysis," or Fresenius's "Quantitative Analysis," or Parnell's Treatise formerly mentioned.

In the case of a body such as sugar, containing only carbon, hydrogen, and oxygen, the amount of carbon being deduced from the weight of carbonic acid, and that of hydrogen from the weight of the water, the amount of oxygen is known by the loss.

Nitrogen.—This element is determined in two ways. 1st. In the free state, as gas, the volume of which is measured, the combustion being conducted as for carbon, in a separate experiment, and the carbonic acid and nitrogen are either passed through strong aqua potassæ, and the nitrogen collected alone over mercury and measured, or, where the proportion of nitrogen is very small, the whole mixed gases are collected over mercury and measured. The carbonic acid being absorbed by a fragment of potash, the nitrogen is left, and its ratio to the carbonic acid is ascertained. In some cases the qualitative method alone is employed. The mixed gases are collected over mercury in five or six tubes in succession, and in each of these the ratio of the two gases is observed. 2nd. In the form of ammonia. The compound is mixed with an excess of a mixture of hydrate of soda and hydrate of lime, and the mixture heated in a combustion tube. In this way the whole nitrogen is converted into ammonia, which is absorbed by hydrochloric acid, in a vessel somewhat similar to the potash apparatus for carbonic acid, devised by Will and Varrentrapp. The hydrochlorate of ammonia is then mixed in a capsule with excess of bichloride of platinum, which converts the ammonia into the sparingly soluble double chloride. The excess of bichloride is removed by washing with a mixture of alcohol and ether, and the salt dried and weighed. Its composition being known, the amount of nitrogen is easily deduced. As a control, the salt may be ignited, and the quantity of nitrogen

calculated again on that of the platinum left. The two calculations should agree. Except in a few peculiar cases, including all those where nitric acid is present, this method is the easiest and the most accurate.

Sulphur.—This element is invariably determined in the form of sulphuric acid, or rather of sulphate of baryta. The compound, such as albumen or taurine, is fused with a mixture of caustic potash and nitre; the mass is dissolved, acidulated, and mixed with a salt of baryta.

In organic chemistry, chlorine only occurs in artificial products, except when as chloride of sodium or potassium it forms part of the ashes. When it is an element in an organic product, the compound is heated in a combustion tube with excess of lime, and the chlorine then determined, as it is in the ashes, in the form of chloride of silver.

The ashes of plants and animals are of course analyzed just as such mixtures would be if occurring in the mineral kingdom. Many improvements have lately been made in the analysis of ashes, but for these we must refer the reader to the scientific journals, where he will find numerous examples of every kind of analysis connected with organic chemistry.

TABLE

*Shewing the Composition of several of the principal Mineral Waters.
(From Dr. Henry's "Elements.")*

[N.B.—The temperature, when not expressed, is to be understood to be 49° or 50° Fahr.]

I. CARBONATED WATERS.

SELTZER. Bergmann.		SPA. Bergmann.	
In each wine pint.		Specific gravity 1·0010.	
		In each wine pint.	
Carbonic Acid	17 cub.in.	Carbonic Acid	13 cub. in.
Specific gravity 1·0027.			
Carbonate of Soda	4 grs.	Carbonate of Soda	1·5 gr.
— of Magnesia	5	— of Magnesia	4·5
— of Lime	3	— of Lime	0·5
Chloride of Sodium	17	Chloride of Sodium	0·2
	29	Oxide of Iron	0·6
			8·3
CARLSBAD. (Temperature 165° Fahr.)		PYRMONT. Bergmann.	
Berzelius.		Specific gravity 1·0024.	
In a wine pint.		In each wine pint.	
Carbonic Acid	5 cub. in.	Carbonic Acid	26 cub. in.
In 1000 parts by weight.			
Sulphate of Soda :	2·58714 grs.	Carbonate of Magnesia	10·0 grs.
Carbonate of Soda	1·25200	— of Lime	4·5
Chloride of Sodium	1·04893	Sulphate of Magnesia	5·5
Carbonate of Lime	0·31219	— of Lime	8·5
Fluoride of Calcium	0·00331	Chloride of Sodium	1·5
Phosphate of Lime	0·00019	Oxide of Iron	0·6
Carbonate of Strontia	0·00097		30·6
— of Magnesia	0·18221		
Phosphate of Alumina	0·00034		
Carbonate of Iron	0·00424		
— of Manganese	a trace.		
Silica	0·07504		
	5·46656		
		POUGES. Hassenfratz.	
		In each wine pint.	
		Carbonic Acid	26 cub. in.
		Carbonate of Soda	10·0 grs.
		— of Magnesia	1·2
		— of Lime	12·0
		Chloride of Sodium	2·2
		Oxide of Iron	2·5
		Silica	0·5
			28·4

Composition of Mineral Waters—Continued.

II. SULPHURETTED WATERS.

AIX-LA-CHAPELLE. Bergmann.

Temperature 143°.

In each wine pint.

Sulphuretted Hydrogen . . . 5.5 cub. in.

Carbonate of Soda 12.00 grs.

of Lime 4.75

Muriate of Soda 5.00

21.75

CHELTENHAM, Sulphur Spring.

Brande and Parkes.

Specific gravity 1.0085.

In each wine pint.

Carbonic Acid 1.5 cub. in.

Sulphuretted Hydrogen . . . 2.5

Sulphate of Soda 23.5 grs.

of Magnesia 5.0

of Lime 1.2

Muriate of Soda 35.0

Oxide of Iron 0.3

65.0

LEAMINGTON, Sulphur Water.

Scudamore.

Specific gravity 1.0042.

Sulphuretted Hydrogen, quantity not ascertained.

In each pint.

Muriate of Soda 15.00 grs.

of Lime 7.96

of Magnesia 3.30

Sulphate of Soda 11.60

Oxide of Iron a trace.

37.86

MOFFAT. Garnet.

Nitrogen 0.5 cub. in.

Carbonic Acid 0.6

Sulphuretted Hydrogen . . . 1.2

Muriate of Soda 4.5 grs.

HARROWGATE WATER.

New Well at the Crown Inn.

(West, Quart. Journ. xv. 82.)

Specific gravity 1.01286 at 69°.

One wine gallon contains

Sulphuretted Hydrogen . . . 6.40 cub. in.

Carbonic Acid 5.25

Azote 6.50

Carburetted Hydrogen . . . 4.65

22.80

Also,

Muriate of Soda 735.00 grs.

of Lime 71.50

of Magnesia 43.00

Bi-carbonate of Soda . . . 14.75

864.25

Old Well.

Sp. gr. 1.01324 at 60°.

Sulphuretted Hydrogen . . . 14.00 cub. in.

Carbonic Acid 4.25

Azotic Gas 3.00

Carburetted Hydrogen . . . 4.15

30.40

Also,

Muriate of Soda 752.00 grs.

of Lime 65.75

of Magnesia 29.20

Bi-carbonate of Soda . . . 12.80

859.75

III. SALINE WATERS.

SEIDLITZ. Bergmann.

Specific gravity 1.0060.

In a pint.

Carbonate of Magnesia 2.5 grs.

of Lime 0.8

Sulphate of Magnesia 130.0

of Lime 5.0

Muriate of Magnesia 4.5

192.8

CHELTENHAM, pure Saline.

Parkes and Brande.

In each pint.

Sulphate of Soda 15.0

of Magnesia 11.0

of Lime 4.5

Muriate of Soda 50.0

80.5

Composition of Mineral Waters—Continued.

LEAMINGTON, Saline. Scudamore.

Specific gravity 1·0119.

In a pint.

Muriate of Soda	53·75
——— of Lime	28·64
——— of Magnesia	20·16
Sulphate of Soda	7·83
Oxide of Iron	a trace.
	110·38

LEAMINGTON, Lord Aylesford's Spring.
Scudamore.

Specific gravity 1·0093.

In a pint.

Muriate of Soda	12·25
——— of Lime	28·24
——— of Magnesia	5·22
Sulphate of Soda	32·96
Oxide of Iron	a trace.
	78·67

BRISTOL. Carrick.

Temp. 74°. Specific gravity 1·00077.

In each pint.

Carbonic Acid	3·5 cub. in.
Carbonate of Lime	1·5 grs.
Sulphate of Soda	1·5
——— of Lime	1·5
Muriate of Soda	0·5
——— of Magnesia	1·0
	6·0

BATH. Phillips.

Temp. 109° to 117°. Sp. gr. 1·002.

In each pint.

Carbonic Acid	1·2 cub. in.
Carbonate of Lime	0·8
Sulphate of Soda	1·4
——— of Lime	9·3
Muriate of Soda	3·4
Silica	0·2
Oxide of Iron	a trace.
	15·1

BATH. Solid contents. Scudamore.

Muriate of Lime	1·2 grs.
——— of Magnesia	1·6
Sulphate of Lime	9·5
——— of Soda	0·9
Silica	0·2
Oxide of Iron	0·01985
Loss, partly Carb. of Soda . .	0·58015
	14·00000

Mr. Cuff has found both Potash and
Iodine in the Bath waters.

BUXTON. Scudamore.

Sp. gr. at 60°, 1·0006. Temp. 82°.

In a wine gallon.

Carbonic Acid	1·50 cub. in.
Nitrogen	4·64
Muriate of Magnesia	0·58 grs.
——— of Soda	2·40
Sulphate of Lime	0·60
Carbonate of Lime	10·40
Extractive and vegetable matter	0·50
Loss	0·52
	15·00

Or, according to Dr. Murray's views.

Sulphate of Soda	0·63
Muriate of Lime	0·57
——— of Soda	1·80
——— of Magnesia	0·58
Carbonate of Lime	10·40
Extract and loss	1·02
	15·00

MATLOCK BATH. Scudamore.

Temp. 68°. Sp. gr. 1·0003.

Free Carbonic Acid.

Muriates and } Magnesia, Lime, and
Sulphates of } Soda?
in very minute quantities not yet ascer-
tained.

Composition of Mineral Waters—Continued.

IV. CHALYBEATE WATERS.

TUNBRIDGE. Scudamore.

Specific gravity 1·0007.

In each gallon.

Muriate of Soda	2·46
— of Lime	0·39
— of Magnesia	0·29
Sulphate of Lime	1·41
Carbonate of Lime	0·27
Oxide of Iron	2·22
Traces of Manganese, Vegetable Fibre, Silica, &c. }	0·44
Loss	0·13
	7·61

CHELTENHAM. Brande and Parkes.

Specific gravity 1·0092.

In a pint.

Carbonic Acid	2·5 cub. in.
Carbonate of Soda	0·5
Sulphate of Soda	22·7
— of Magnesia	6·0
— of Lime	2·5
Muriate of Soda	41·3
Oxide of Iron	0·8
	73·8

BRIGHTON. Marcet.

Specific gravity 1·00108.

Carbonic Acid Gas	2½ cub. in.
Sulphate of Iron	1·80 grs.
— of Lime	4·09
Muriate of Soda	1·53
— of Magnesia	0·75
Silica	0·14
Loss	0·19
	8·50

HARROWGATE, Oddie's Chalybeate.

Scudamore.

Specific gravity 1·0053.

In each gallon.

Muriate of Soda	300·40
— of Lime	22·00
— of Magnesia	9·90
Sulphate of Lime	1·86
Carbonate of Lime	6·70
— of Magnesia	0·80
Oxide of Iron	2·40
Residue, chiefly Silica	0·40
	344·46

APPENDIX.

TABLE I.

Table of Chemical Equivalents of Elementary Substances.

Elements.	Equiv ^t .	Elements.	Equiv ^t .	Elements.	Equiv ^t .
Aluminium .	13·7	Gold	199·2	Potassium .	39·26
Antimony .	129·2	Hydrogen . .	1	Rhodium . .	52·2
Arsenic . .	75·4	Iodine . . .	126·3	Selenium . .	39·6
Barium . .	68·7	Iridium . . .	98·8	Silicium . .	22·5
Bismuth . .	71	Iron	27·2	Silver	108
Boron . . .	10·9	Lead	103·6	Sodium . . .	23·3
Bromine . .	78·4	Lithium . .	6	Strontium .	43·8
Cadmium . .	55·8	Magnesium .	12·7	Sulphur . .	16·1
Calcium . .	20·5	Manganese .	27·7	Tellurium .	64·2
Carbon . . .	6·04	Mercury . .	202	Thorium . .	59·6
Cerium . . .	46	Molybdenum	47·7	Tin	57·9
Chlorine . .	35·47	Nickel . . .	29·5	Titanium . .	24·3
Chromium .	28	Nitrogen . .	14·15	Tungsten . .	99·7
Cobalt . . .	29·5	Osmium . .	99·7	Vanadium .	68·5
Columbium .	185	Oxygen . .	8	Uranium . .	217
Copper . . .	31·6	Palladium .	53·3	Yttrium . .	32·2
Fluorine . .	18·68	Phosphorus .	31·4	Zinc	32·3
Glucinium .	26·5	Platinum . .	98·8	Zirconium .	33·7

II. — *TABLE of the elastic Force of Aqueous Vapour at different Temperatures, expressed in Inches of Mercury.*

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
32°F.	0·200	0·200	79°F.	0·971		126°F.	3·89	
33	0·207		80	1·00	1·010	127	4·00	
34	0·214		81	1·04		128	4·11	
35	0·221		82	1·07		129	4·22	
36	0·229		83	1·10		130	4·34	4·366
37	0·237		84	1·14		131	4·47	
38	0·245		85	1·17	1·170	132	4·60	
39	0·254		86	1·21		133	4·73	
40	0·263	0·250	87	1·24		134	4·86	
41	0·273		88	1·28		135	5·00	5·070
42	0·283		89	1·32		136	5·14	
43	0·294		90	1·36	1·360	137	5·29	
44	0·305		91	1·40		138	5·44	
45	0·316		92	1·44		139	5·59	
46	0·328		93	1·48		140	5·74	5·770
47	0·339		94	1·53		141	5·90	
48	0·351		95	1·58	1·640	142	6·05	
49	0·363		96	1·63		143	6·21	
50	0·375	0·360	97	1·68		144	6·37	
51	0·388		98	1·74		145	6·53	6·600
52	0·401		99	1·80		146	6·70	
53	0·415		100	1·86	1·860	147	6·87	
54	0·429		101	1·92		148	7·05	
55	0·443	0·416	102	1·98		149	7·23	
56	0·458		103	2·04		150	7·42	7·530
57	0·474		104	2·11		151	7·61	
58	0·490		105	2·18	2·100	152	7·81	
59	0·507		106	2·25		153	8·01	
60	0·524	0·516	107	2·32		154	8·20	
61	0·542		108	2·39		155	8·40	8·500
62	0·560		109	2·46		156	8·60	
63	0·578		110	2·53	2·456	157	8·81	
64	0·597		111	2·60		158	9·02	
65	0·616	0·630	112	2·68		159	9·24	
66	0·635		113	2·76		160	9·46	9·600
67	0·655		114	2·84		161	9·68	
68	0·676		115	2·92	3·820	162	9·91	
69	0·698		116	3·00		163	10·15	
70	0·721	0·726	117	3·08		164	10·41	
71	0·745		118	3·16		165	10·63	10·800
72	0·770		119	3·25		166	10·96	
73	0·796		120	3·33	2·300	167	11·25	
74	0·823		121	3·42		168	11·54	
75	0·851	0·860	122	3·50		169	11·83	
76	0·880		123	3·59		170	12·13	12·050
77	0·910		124	3·69		171	12·43	
78	0·940		125	3·79	3·830	172	12·73	

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
173°F.	13.02		224°F.	37.53		275°F.	83.13	93.480
174	13.32		225	38.20	39.110	276	84.35	
175	13.62	13.550	226	38.89	40.100	277	85.47	97.800
176	13.92		227	39.59		278	86.50	
177	14.22		228	40.30		279	87.63	101.600
178	14.52		229	41.02		280	88.75	101.900
179	14.83		230	41.75	43.100	281	89.87	104.400
180	15.15	15.160	231	42.49		282	90.99	
181	15.50		232	43.24		283	92.11	107.700
182	15.86		233	44.00		284	93.23	
183	16.23		234	44.78	46.800	285	94.35	112.200
184	16.61		235	45.58	47.220	286	95.48	
185	17.00	16.900	236	46.39		287	96.64	114.800
186	17.40		237	47.20		288	97.80	
187	17.80		238	48.02	50.300	289	98.96	118.200
188	18.20		239	48.84		290	100.12	120.150
189	18.60		240	49.67	51.700	291	101.28	
190	19.00	19.000	241	50.50		292	102.45	123.100
191	19.42		242	51.34	53.600	293	103.63	
192	19.86		243	52.18		294	104.80	126.700
193	20.32		244	53.03		295	105.97	129.000
194	20.77		245	53.88	56.340	296	107.14	
195	21.22	21.100	246	54.68		297	108.31	133.900
196	21.68		247	55.54		298	109.48	137.400
197	22.13		248	56.42	60.400	299	110.64	
198	22.69		249	57.31		300	111.81	139.700
199	23.16		250	58.21	61.900	301	112.98	
200	23.64	23.600	251	59.12	63.500	302	114.15	144.300
201	24.12		252	60.05		303	115.32	147.700
202	24.61		253	61.00		304	116.50	
203	25.10		254	61.92	66.700	305	117.68	150.560
204	25.61		255	62.85	67.250	306	118.86	154.400
205	26.13	25.900	256	63.76		307	120.03	
206	26.66		257	64.82	69.800	308	121.20	157.700
207	27.20		258	65.78		309	122.37	
208	27.74		259	66.75		310	123.53	161.300
209	28.29		260	67.73	72.300	311	124.69	164.800
210	28.84	28.880	261	68.72		312	125.85	167.000
211	29.41		262	69.72	75.900	313	127.00	
212	30.00	30.000	263	70.73		314	128.15	
213	30.60		264	71.74	77.900	315	129.29	
214	31.21		265	72.76	78.040	316	130.43	
215	31.83		266	73.77		317	131.57	
216	32.46	33.400	267	74.79	81.900	318	132.72	
217	33.09		268	75.80		319	133.86	
218	33.72		269	76.82	84.900	320	135.00	
219	34.35		270	77.85	86.300	321	136.14	
220	34.99	35.540	271	78.89	88.000	322	137.28	
221	35.63	36.700	272	79.94		323	138.42	
222	36.25		273	80.98	91.200	324	139.56	
223	36.88		274	82.01		325	140.70	

TABLE III.

Dr. Ure's Table, shewing the elastic Force of the Vapours of Alcohol, Ether, Oil of Turpentine, and Petroleum or Naphtha, at different Temperatures, expressed in Inches of Mercury.

Ether.		Alcohol sp. gr. 0·813.		Alcohol sp. gr. 0·813.		Petroleum.	
Temp.	Force of Vapour.	Temp.	Force of Vapour.	Temp.	Force of Vapour.	Temp.	Force of Vapour.
34°	6·20	32°	0·40	193·3°	46·60	316°	30·00
44	8·10	40	0·56	196·3	50·10	320	31·70
54	10·30	45	0·70	200	53·00	325	34·00
64	10·00	50	0·86	206	60·10	330	36·40
74	16·10	55	1·00	210	65·00	335	38·90
84	20·00	60	1·23	214	69·30	340	41·60
94	24·70	65	1·49	216	72·20	345	44·10
104	30·00	70	1·76	220	78·50	350	46·86
105	30·00	75	2·10	225	87·50	355	50·20
110	32·54	80	2·45	230	94·10	360	53·30
115	35·90	85	2·93	232	97·10	365	56·90
120	39·47	90	3·40	236	103·60	370	60·70
125	43·24	95	3·90	238	106·90	372	61·90
130	47·14	100	4·50	240	111·24	375	64·00
135	51·90	105	5·20	244	118·20	Oil of Turpentine.	
140	56·90	110	6·00	247	122·10		
145	62·10	115	7·10	248	126·10	Temp.	Force of Vapour.
150	67·60	120	8·10	249·7	131·40		
155	73·60	125	9·25	250	132·30	304°	30·00
160	80·30	130	10·60	252	138·60	307·6	32·60
165	86·40	135	12·15	254·3	143·70	310	33·50
170	92·80	140	13·90	258·6	151·60	315	35·20
175	99·10	145	15·95	260	155·20	320	37·06
180	108·30	150	18·00	262	161·40	322	37·80
185	116·10	155	20·30	264	166·10	326	40·20
190	124·80	160	22·60			330	42·10
195	133·70	165	25·40			336	45·00
200	142·80	170	28·30			340	47·30
205	151·30	173	30·00			343	49·40
210	166·00	178·3	33·50			347	51·70
		180	34·73			350	53·80
		182·3	36·40			354	56·60
		185·3	39·90			357	58·70
		190	43·20			360	60·80
						362	62·40

TABLE IV.

For the Conversion of Degrees on the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50°	—58° 0	—6°	21° 2	38°	100° 4	82°	179° 6
—49	—56.2	—5	23.0	39	102.2	83	181.4
—48	—54.4	—4	24.8	40	104.0	84	183.2
—47	—52.6	—3	26.6	41	105.8	85	185.0
—46	—50.8	—2	28.4	42	107.6	86	186.8
—45	—49.0	—1	30.2	43	109.4	87	188.6
—44	—47.2	0	32.0	44	111.2	88	190.4
—43	—45.4	+1	33.8	45	113.0	89	192.2
—42	—43.6	2	35.6	46	114.8	90	194.0
—41	—41.8	3	37.4	47	116.6	91	195.8
—40	—40.0	4	39.2	48	118.4	92	197.6
—39	—38.2	5	41.0	49	120.2	93	199.4
—38	—36.4	6	42.8	50	122.0	94	201.2
—37	—34.6	7	44.6	51	123.8	95	203.0
—36	—32.8	8	46.4	52	125.6	96	204.8
—35	—30.0	9	48.2	53	127.4	97	206.6
—34	—29.2	10	50.0	54	129.2	98	208.4
—33	—27.4	11	51.8	55	131.0	99	210.2
—32	—25.6	12	53.6	56	132.8	100	212.0
—31	—23.8	13	55.4	57	134.6	101	213.8
—30	—22.0	14	57.2	58	136.4	102	215.6
—29	—20.2	15	59.0	59	138.2	103	217.4
—28	—18.4	16	60.8	60	140.0	104	219.2
—27	—16.6	17	62.6	61	141.8	105	221.0
—26	—14.8	18	64.4	62	143.6	106	222.8
—25	—13.0	19	66.2	63	145.4	107	224.6
—24	—11.2	20	68.0	64	147.2	108	226.4
—23	—9.4	21	69.8	65	149.0	109	228.2
—22	—7.6	22	71.6	66	150.8	110	230.0
—21	—5.8	23	73.4	67	152.6	111	231.8
—20	—4.0	24	75.2	68	154.4	112	233.6
—19	—2.2	25	77.0	69	156.2	113	235.4
—18	—0.4	26	78.8	70	158.0	114	237.2
—17	+1.4	27	80.6	71	159.8	115	239.0
—16	3.2	28	82.4	72	161.6	116	240.8
—15	5.0	29	84.2	73	163.4	117	242.6
—14	6.8	30	86.0	74	165.2	118	244.4
—13	8.6	31	87.8	75	167.0	119	246.2
—12	10.4	32	89.6	76	168.8	120	248.0
—11	12.2	33	91.4	77	170.6	121	249.8
—10	14.0	34	93.2	78	172.4	122	251.6
—9	15.8	35	95.0	79	174.2	123	253.4
—8	17.6	36	96.8	80	176.0	124	255.2
—7	19.4	37	98.6	81	177.8	125	257.0

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
126°	258° 8	175°	347° 0	224°	435° 2	273°	523° 4
127	260.6	176	348.8	225	437.0	274	525.2
128	262.4	177	350.6	226	438.8	275	527.0
129	264.2	178	352.4	227	440.6	276	528.8
130	266.0	179	354.2	228	442.4	277	530.6
131	267.8	180	356.0	229	444.2	278	532.4
132	269.6	181	357.8	230	446.0	279	534.2
133	271.4	182	359.6	231	447.8	280	536.0
134	273.2	183	361.4	232	449.6	281	537.8
135	275.0	184	363.2	233	451.4	282	539.6
136	276.8	185	365.0	234	453.2	283	541.4
137	278.6	186	366.8	235	455.0	284	543.2
138	280.4	187	368.6	236	456.8	285	545.0
139	282.2	188	370.4	237	458.6	286	546.8
140	284.0	189	372.2	238	460.4	287	548.6
141	285.8	190	374.0	239	462.2	288	550.4
142	287.6	191	375.8	240	464.0	289	552.2
143	289.4	192	377.6	241	465.8	290	554.0
144	291.2	193	379.4	242	467.6	291	555.8
145	293.0	194	381.2	243	469.4	292	557.6
146	294.8	195	383.0	244	471.2	293	559.4
147	296.6	196	384.8	245	473.0	294	561.2
148	298.4	197	386.6	246	474.8	295	563.0
149	300.2	198	388.4	247	476.6	296	564.8
150	302.0	199	390.2	248	478.4	297	566.6
151	303.8	200	392.0	249	480.2	298	568.4
152	305.6	201	393.8	250	482.0	299	570.2
153	307.4	202	395.6	251	483.8	300	572.0
154	309.2	203	397.4	252	485.6	301	573.8
155	311.0	204	399.2	253	487.4	302	575.6
156	312.8	205	401.0	254	489.2	303	577.4
157	314.6	206	402.8	255	491.0	304	579.2
158	316.4	207	404.6	256	492.8	305	581.0
159	318.2	208	406.4	257	494.6	306	582.8
160	320.0	209	408.2	258	496.4	307	584.6
161	321.8	210	410.0	259	498.2	308	586.4
162	323.6	211	411.8	260	500.0	309	588.2
163	325.4	212	413.6	261	501.8	310	590.0
164	327.2	213	415.4	262	503.6	311	591.8
165	329.0	214	417.2	263	505.4	312	593.6
166	330.8	215	419.0	264	507.2	313	595.4
167	332.6	216	420.8	265	509.0	314	597.2
168	334.4	217	422.6	266	510.8	315	599.0
169	336.2	218	424.4	267	512.6	316	600.8
170	338.0	219	426.2	268	514.4	317	602.6
171	339.8	220	428.0	269	516.2	318	604.4
172	341.6	221	429.8	270	518.0	319	606.2
173	343.4	222	431.6	271	519.8	320	608.0
174	345.2	223	433.4	272	521.6		

TABLE V.

Dr. Ure's Table of the Quantity of Oil of Vitriol, of sp. gr. 1·8485, and of Anhydrous Acid, in 100 Parts of dilute Sulphuric Acid, at different Densities.

Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.
100	1·8485	81·54	66	1·5503	53·82	32	1·2334	26·09
99	1·8475	80·72	65	1·5390	53·00	31	1·2260	25·28
98	1·8460	79·90	64	1·5280	52·18	30	1·2184	24·46
97	1·8439	79·09	63	1·5170	51·37	29	1·2108	23·65
96	1·8410	78·28	62	1·5066	50·55	28	1·2032	22·83
95	1·8376	77·46	61	1·4960	49·74	27	1·1956	22·01
94	1·8336	76·65	60	1·4860	48·92	26	1·1876	21·20
93	1·8290	75·83	59	1·4760	48·11	25	1·1792	20·38
92	1·8233	75·02	58	1·4660	47·29	24	1·1706	19·57
91	1·8179	74·20	57	1·4560	46·48	23	1·1626	18·75
90	1·8115	73·39	56	1·4460	45·66	22	1·1549	17·94
89	1·8043	72·57	55	1·4360	44·85	21	1·1480	17·12
88	1·7962	71·75	54	1·4265	44·03	20	1·1410	16·31
87	1·7870	70·94	53	1·4170	43·22	19	1·1330	15·49
86	1·7774	70·12	52	1·4073	42·40	18	1·1246	14·68
85	1·7673	69·31	51	1·3977	41·58	17	1·1165	13·86
84	1·7570	68·49	50	1·3884	40·77	16	1·1090	13·05
83	1·7465	67·68	49	1·3788	39·95	15	1·1019	12·23
82	1·7360	66·86	48	1·3697	39·14	14	1·0953	11·41
81	1·7245	66·05	47	1·3612	38·32	13	1·0887	10·60
80	1·7120	65·23	46	1·3530	37·51	12	1·0809	9·78
79	1·6993	64·42	45	1·3440	36·69	11	1·0743	8·97
78	1·6870	63·60	44	1·3345	35·88	10	1·0682	8·15
77	1·6750	62·78	43	1·3255	35·06	9	1·0614	7·34
76	1·6630	61·97	42	1·3165	34·25	8	1·0544	6·52
75	1·6520	61·15	41	1·3080	33·43	7	1·0477	5·71
74	1·6415	60·34	40	1·2999	32·61	6	1·0405	4·89
73	1·6321	59·52	39	1·2913	31·80	5	1·0336	4·08
72	1·6204	58·71	38	1·2826	30·98	4	1·0268	3·26
71	1·6090	57·89	37	1·2740	30·17	3	1·0206	2·446
70	1·5975	57·08	36	1·2654	29·35	2	1·0140	1·63
69	1·5868	56·26	35	1·2572	28·54	1	1·0074	0·8154
68	1·5760	55·45	34	1·2490	27·72			
67	1·5648	54·63	33	1·2409	26·91			

TABLE VI.

*Dr. Ure's Table of the Quantity of Real or Anhydrous Nitric Acid
in 100 Parts of Liquid Acid, at different Densities.*

Specific Gravity.	Real Acid in 100 Parts of the Liquid.	Specific Gravity.	Real Acid in 100 Parts of the Liquid.	Specific Gravity.	Real Acid in 100 Parts of the Liquid.
1.5000	79.700	1.3783	52.602	1.1895	26.301
1.4980	78.903	1.3732	51.805	1.1833	25.504
1.4960	78.106	1.3681	51.068	1.1770	24.707
1.4940	77.309	1.3630	50.211	1.1709	23.910
1.4910	76.512	1.3579	49.414	1.1648	23.113
1.4880	75.715	1.3529	48.617	1.1587	22.316
1.4850	74.918	1.3477	47.820	1.1526	21.519
1.4820	74.121	1.3427	47.023	1.1465	20.722
1.4790	73.324	1.3376	46.226	1.1403	19.925
1.4760	72.527	1.3323	45.429	1.1345	19.128
1.4730	71.730	1.3270	44.632	1.1286	18.331
1.4700	70.933	1.3216	43.835	1.1227	17.534
1.4670	70.136	1.3163	43.038	1.1168	16.737
1.4640	69.339	1.3110	42.241	1.1109	15.940
1.4600	68.542	1.3056	41.444	1.1051	15.143
1.4570	67.745	1.3001	40.647	1.0993	14.346
1.4530	66.948	1.2947	39.850	1.0935	13.549
1.4500	66.155	1.2887	39.053	1.0878	12.752
1.4460	65.354	1.2826	38.256	1.0821	11.955
1.4424	64.557	1.2765	37.459	1.0764	11.158
1.4385	63.760	1.2705	36.662	1.0708	10.361
1.4346	62.963	1.2644	35.865	1.0651	9.564
1.4306	62.166	1.2583	35.068	1.0595	8.767
1.4269	61.369	1.2523	34.271	1.0540	7.970
1.4228	60.572	1.2462	33.474	1.0485	7.173
1.4189	59.775	1.2402	32.677	1.0430	6.376
1.4147	58.978	1.2341	31.880	1.0375	5.579
1.4107	58.181	1.2277	31.083	1.0320	4.782
1.4065	57.384	1.2212	30.286	1.0267	3.985
1.4023	56.587	1.2148	29.489	1.0212	3.188
1.3978	55.790	1.2084	28.692	1.0159	2.391
1.3945	54.993	1.2019	27.895	1.0106	1.594
1.3882	54.196	1.1958	27.098	1.0053	0.797
1.3833	53.399				

VII.—*Table of Lowitz, shewing the Quantity of absolute Alcohol in Spirits of different Specific Gravities.*

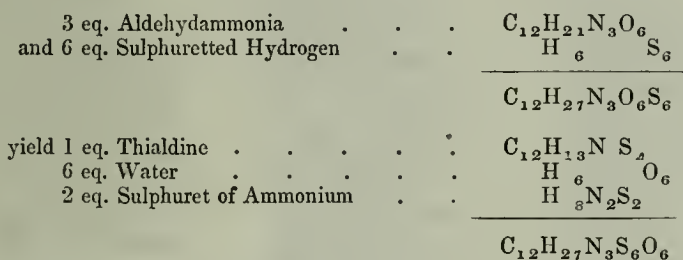
100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.	
Alc.	Wat.	At 68°.	At 60°.	Alc.	Wat.	At 68°.	At 60°.	Alc.	Wat.	At 68°.	At 60°.
100	0	0.791	0.796	66	34	0.877	0.881	32	68	0.952	0.955
99	1	0.794	0.798	65	35	0.880	0.883	31	69	0.954	0.957
98	2	0.797	0.801	64	36	0.882	0.886	30	70	0.956	0.958
97	3	0.800	0.804	63	37	0.885	0.889	29	71	0.957	0.960
96	4	0.803	0.807	62	38	0.887	0.891	28	72	0.959	0.962
95	5	0.805	0.809	61	39	0.889	0.893	27	73	0.961	0.963
94	6	0.808	0.812	60	40	0.892	0.896	26	74	0.963	0.965
93	7	0.811	0.815	59	41	0.894	0.898	25	75	0.965	0.967
92	8	0.813	0.817	58	42	0.896	0.900	24	76	0.966	0.968
91	9	0.816	0.820	57	43	0.899	0.902	23	77	0.968	0.970
90	10	0.818	0.822	56	44	0.901	0.904	22	78	0.970	0.972
89	11	0.821	0.825	55	45	0.903	0.906	21	79	0.971	0.973
88	12	0.823	0.827	54	46	0.905	0.908	20	80	0.973	0.974
87	13	0.826	0.830	53	47	0.907	0.910	19	81	0.974	0.975
86	14	0.828	0.832	52	48	0.909	0.912	18	82	0.976	0.977
85	15	0.831	0.835	51	49	0.912	0.915	17	83	0.977	0.978
84	16	0.834	0.838	50	50	0.914	0.917	16	84	0.978	0.979
83	17	0.836	0.840	49	51	0.917	0.920	15	85	0.980	0.981
82	18	0.839	0.843	48	52	0.919	0.922	14	86	0.981	0.982
81	19	0.842	0.846	47	53	0.921	0.924	13	87	0.983	0.984
80	20	0.844	0.848	46	54	0.923	0.926	12	88	0.985	0.986
79	21	0.847	0.851	45	55	0.925	0.928	11	89	0.986	0.987
78	22	0.849	0.853	44	56	0.927	0.930	10	90	0.987	0.988
77	23	0.851	0.855	43	57	0.930	0.933	9	91	0.988	0.989
76	24	0.853	0.857	42	58	0.932	0.935	8	92	0.989	0.990
75	25	0.856	0.860	41	59	0.934	0.937	7	93	0.991	0.991
74	26	0.859	0.863	40	60	0.936	0.939	6	94	0.992	0.992
73	27	0.861	0.865	39	61	0.938	0.941	5	95	0.994	
72	28	0.863	0.867	38	62	0.940	0.943	4	96	0.995	
71	29	0.866	0.870	37	63	0.942	0.945	3	97	0.997	
70	30	0.868	0.872	36	64	0.944	0.947	2	98	0.998	
69	31	0.870	0.874	35	65	0.946	0.949	1	99	0.999	
68	32	0.872	0.875	34	66	0.948	0.951	0	100	1.000	
67	33	0.875	0.879	33	67	0.950	0.953				

VIII.—*Tables shewing the Specific Gravity of Liquids at the Temperature of 55° Fahr., corresponding to the Degrees of Beaumé's Hydrometer.*

FOR LIQUIDS LIGHTER THAN WATER.									
Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10	1.000	17	0.949	23	0.909	29	0.874	35	0.842
11	0.990	18	0.942	24	0.903	30	0.867	36	0.837
12	0.985	19	0.935	25	0.897	31	0.861	37	0.832
13	0.977	20	0.928	26	0.892	32	0.856	38	0.827
14	0.970	21	0.922	27	0.886	33	0.852	39	0.822
15	0.963	22	0.915	28	0.880	34	0.847	40	0.817
16	0.955								
FOR LIQUIDS HEAVIER THAN WATER.									
Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
0	1.000	15	1.114	30	1.261	45	1.455	60	1.717
3	1.020	18	1.140	33	1.295	48	1.500	63	1.779
6	1.040	21	1.170	36	1.333	51	1.547	66	1.848
9	1.064	24	1.200	39	1.373	54	1.594	69	1.920
12	1.089	27	1.230	42	1.414	57	1.659	72	2.000

ADDENDUM.

Thialdine.—Liebig and Wöhler have very recently discovered that when an aqueous solution of aldehydammonia is acted on by sulphuretted hydrogen, a little ammonia being previously added, crystals of a new compound are deposited, which has basic properties, and has been called *Thialdine*. It is produced by the action of 3 eq. of aldehydammonia on 6 eq. of sulphuretted hydrogen. Thus:—



Thialdine is almost insoluble in water, but very soluble in alcohol and ether. It is deposited, by spontaneous evaporation, from its etherial solution, in large and beautiful crystals, resembling camphor. It is very volatile and fusible, has an unpleasant aromatic smell, and is a powerful base, neutralizing the strongest acids, and forming beautiful crystalline salts. When heated with hydrate of lime, thialdine yields *leucoline* or *quinoline*, one of the volatile bases of coal-tar.

When aldehydammonia is acted on by seleniuretted hydrogen, an analogous basic compound, *selenaldine*, is formed; and it appears probable, from the experiments of Liebig and Wöhler, that telluretted hydrogen is capable also of yielding a similar compound.

THE THEORY OF THE CONJUGATE FUNCTIONS

Let $u(x, y)$ and $v(x, y)$ be two functions of x and y which satisfy the Cauchy-Riemann equations

$$u_x = v_y, \quad u_y = -v_x.$$

Then the function $f(z) = u + iv$ is analytic in the region where u and v are defined. Conversely, if $f(z)$ is analytic, then u and v satisfy the Cauchy-Riemann equations. The functions u and v are called conjugate functions.

Let $z = x + iy$ and $\bar{z} = x - iy$. Then the Cauchy-Riemann equations can be written in the form

$$\frac{\partial f}{\partial \bar{z}} = 0.$$

where $f = u + iv$. This shows that f is a function of z alone.

Let u and v be conjugate functions. Then u is harmonic, i.e. it satisfies Laplace's equation $\nabla^2 u = 0$. Similarly, v is harmonic. Conversely, if u is harmonic, then there exists a function v such that $u + iv$ is analytic. The function v is called the conjugate function of u .

Let u and v be conjugate functions. Then the function $f(z) = u + iv$ is analytic. The function f is called the analytic function corresponding to u and v .

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